Chapter

3.2

Page 1:

Alright everyone, welcome back to Physics 608, Laser Spectroscopy. Today, we embark on a crucial topic within the broader theme of spectral line shapes: Chapter 3, Section 2, focusing on **Doppler Width**. Understanding Doppler broadening is absolutely fundamental to interpreting spectroscopic data, especially in gaseous media, and it forms a cornerstone of many diagnostic techniques.

As you can see, this material was prepared by Distinguished Professor Doctor M A Gondal for this course. Let's delve into why the widths of spectral lines, and particularly the Doppler contribution to these widths, are so important.

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So, let's start with the basics of **Spectral Lines – Why Widths Matter**.

The first point on this slide reminds us of an idealized scenario: "A 'spectral line' ideally marks a single, sharply-defined transition energy between two quantum states." Think about the Bohr model, or more sophisticated quantum mechanical descriptions of atoms and molecules. We have discrete energy levels, say E_{one} and E_{two}. A transition between these states corresponds to the absorption or emission of a photon with energy $h\nu$ precisely equal to the energy difference, $\Delta E = E_{\text{two}} - E_{\text{one}}$. In this perfect world, if you plotted the absorption or emission intensity as a function of frequency, you'd see an infinitely sharp spike, a delta function, right at the resonant frequency $\nu_{\text{zero}} = \frac{\Delta E}{h}$. This would be a perfectly defined spectral line.

However, as the second bullet point states: "In real experiments each line possesses a finite width, i.e. light is emitted/absorbed over a band of angular frequencies ω." Nature, as it turns out, is a bit more nuanced. We never observe these infinitely sharp lines. Instead, we see a profile, a distribution of intensities centered around ω_{zero} (the angular frequency corresponding to ν_{zero}), but spread out over a range of frequencies. This spread is what we call the linewidth. So, instead of a single frequency, there's a whole band of frequencies involved in the interaction.

Why is this important? The third bullet point gives us the crucial insight: "Width carries information about underlying physical processes (lifetimes, motion, collisions, external fields, ...)." This is where spectroscopy becomes truly powerful as a diagnostic tool. The shape and width of a spectral line are not just nuisance effects; they are fingerprints of the environment and the dynamics of the atoms or molecules we are studying.

* **Lifetimes:** The finite lifetime of an excited state, due to spontaneous emission, leads to what's called natural broadening. This is a fundamental quantum mechanical effect, linked to the Heisenberg Uncertainty Principle. A shorter lifetime means a larger uncertainty in energy, and thus a broader line. * **Motion:** This is the main topic for today – Doppler broadening. If the atoms or molecules are moving, their apparent resonant frequency will be shifted relative to a stationary observer or a light source. Since we typically deal with an ensemble of particles moving with a distribution of velocities (like the Maxwell-Boltzmann distribution in a gas), this results in a distribution of observed frequencies, effectively broadening the spectral line. * **Collisions:** Atoms or molecules in a gas are constantly colliding. These collisions can interrupt the process of light emission or absorption, or perturb the energy levels. This leads to collisional broadening, also known as pressure broadening, because the collision rate typically increases with pressure. * **External fields:** The presence of electric fields (Stark effect) or magnetic fields (Zeeman effect) can split or shift energy levels, leading to more complex line structures that can also be interpreted as a form of broadening if the individual components are not resolved.

So, by carefully analyzing the line shape and extracting the width, we can learn about these fundamental physical processes.

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Following on from that, the **Goal of this unit** is clearly stated: "build a step-by-step, quantitative understanding of the Doppler contribution to the linewidth and place it in context with other mechanisms."

So, our journey today will be to first understand the physics of the Doppler effect as it applies to atoms and molecules interacting with light. Then, we will see how the thermal motion of these particles, characterized by a velocity distribution, translates into a specific line shape – the Gaussian profile. We'll derive expressions for the Doppler width, understand its dependence on parameters like temperature and mass, and finally, we'll discuss how this Doppler broadening combines with other broadening mechanisms, like the natural or collisional broadening we just mentioned, to give the overall observed line shape, often described by a Voigt profile. This quantitative understanding is essential for accurately interpreting spectra and extracting meaningful physical parameters.

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Now, let's visualize what we're talking about with this slide titled "Chap. 3.2 Doppler Width: Spectral Lines – Why Widths Matter," which shows a **Schematic of an Ideal vs. Real Spectral Line Profiles.**

On the graph, the vertical axis is labeled $I(\omega)$ (capital I of omega), representing the intensity or strength of the spectral line as a function of angular frequency ω on the horizontal axis. The center of the line, ω_{zero}, is at the origin of this relative frequency axis, so omega here is really the detuning from the line center.

The legend describes four different profiles:

* First, we have the **Ideal (**δ-function), shown as a dashed black vertical line spiking up at $\omega = 0$. This represents that idealized, infinitely sharp spectral line we discussed. It has all its intensity at a single frequency. Of course, this is a mathematical idealization, not physically observed.

* Next, we see a **Lorentzian** profile, plotted as a solid blue line. Notice its characteristic shape: it's peaked at the center, but its "wings" – the parts of the line far from the center – fall off relatively slowly. As we'll recap shortly, this shape is typically associated with natural broadening (due to finite lifetimes) and collisional broadening.

* Then, there's a **Gaussian** profile, shown as a solid orange line. This also peaks at the center, but its wings fall off much more rapidly than the Lorentzian. As we will spend much of today deriving, this Gaussian shape is characteristic of Doppler broadening in a thermal gas.

* Finally, the **Voigt Profile** is shown as a solid green line. Observe that the Voigt profile often looks somewhat like a Gaussian near its center but can exhibit broader wings, more akin to a Lorentzian, further out. This is because the Voigt profile is, in fact, a convolution of a Gaussian profile and a Lorentzian profile. It represents the line shape when both inhomogeneous broadening (like Doppler) and homogeneous broadening (like natural or collisional) are simultaneously present and significant.

This graph provides a great visual summary. Our ideal is the delta function, but reality gives us broadened profiles like Lorentzians, Gaussians, or, most generally, Voigts. Our focus today is to deeply understand the origin and characteristics of the Gaussian component arising from Doppler broadening.

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Alright, before we dive deep into Doppler broadening, let's do a quick **Natural (Lifetime) Broadening Recap**. This is often referred to as homogeneous broadening because it affects all atoms or molecules in the ensemble in the same way.

The first bullet point gets to the **Origin**: "finite excited-state lifetime τ (tau) gives an energy uncertainty ΔE (Delta E) approximately equal to $\frac{\hbar}{2\tau}$ (h-bar over two tau)." This is a direct consequence of the Heisenberg Uncertainty

Principle, specifically the energy-time uncertainty relation, $\Delta E\,\Delta t \geq \frac{\hbar}{2}$. If an excited state has an average lifetime τ, then Δt can be associated with τ. The energy of that state, and therefore the energy of a photon emitted from it, will have an inherent uncertainty, or spread, ΔE. The factor of 2 in 2τ arises from considering the full width of the energy distribution. This energy uncertainty ΔE directly translates into a frequency spread $\Delta\omega$ (Delta omega) because $E = \hbar\omega$, so $\Delta E = \hbar\Delta\omega$. Thus, $\Delta\omega$ is on the order of $\frac{1}{\tau}$.

The second bullet tells us the consequence for the line shape: "Resulting **Lorentzian profile** for emitted intensity." When an ensemble of atoms undergoes spontaneous emission from an excited state with lifetime τ, the spectral line shape is given by a Lorentzian function. The formula shown is:

$$I_{\text{nat}}(\omega) = I_0 \cdot \frac{\left(\frac{\gamma}{2}\right)^2}{(\omega - \omega_0)^2 + \left(\frac{\gamma}{2}\right)^2}$$

Let's break this down: * $I_{\text{nat}}(\omega)$ (capital I sub nat of omega) is the intensity of natural emission as a function of angular frequency ω. * I_0 (capital I sub zero) is the peak intensity, occurring at $\omega = \omega_0$. * ω_0 (omega naught) is the central angular frequency of the transition, corresponding to the exact energy difference between the states without any uncertainty. * γ (gamma) is a crucial parameter here, representing the decay rate. * The term $(\omega - \omega_0)$ is the detuning from the line center. Notice it's squared in the denominator, making the profile symmetric around ω_0. * The term $\left(\frac{\gamma}{2}\right)^2$ in the denominator is added to the squared detuning. This term determines the width of the Lorentzian. When the detuning $(\omega - \omega_0)$ equals $\pm\frac{\gamma}{2}$, the denominator becomes $2 \cdot \left(\frac{\gamma}{2}\right)^2$, so the intensity $I_{\text{nat}}(\omega)$ drops to $\frac{I_0}{2}$, which is half its peak value.

The third bullet point defines this decay rate gamma: "$\gamma = \frac{1}{\tau}$ – radiative decay rate (units: s^{-1} (inverse seconds))."

Finally, the slide mentions the "Full width at half maximum (FWHM):". We'll see the expression for this on the next page, but based on our discussion of the Lorentzian formula, you can probably already guess what it will be.

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Continuing our recap of natural broadening, the first thing we see is the expression for the Full Width at Half Maximum, or FWHM, for this natural Lorentzian lineshape. It is given by:

$$\delta\omega_{\mathrm{n}} = \gamma$$

This confirms what we deduced on the previous page. The FWHM, which is the difference between the two angular frequencies at which the intensity is half its maximum value, is exactly equal to γ, the radiative decay rate, which is $\frac{1}{\tau}$. So, $\delta\omega_{\mathrm{n}} = \frac{1}{\tau}$. This makes intuitive sense: a shorter lifetime τ leads to a larger decay rate γ, and thus a larger linewidth $\delta\omega_{\mathrm{n}}$. This natural linewidth is the minimum possible linewidth a transition can have, limited only by the quantum nature of spontaneous emission.

Now, a **Key point** about the Lorentzian profile is highlighted: "Lorentzian wings decay slowly $\propto \frac{1}{(\omega-\omega_0)^2}$." As you move away from the line center (ω_0), so as the detuning ($\omega - \omega_0$) becomes large, the intensity decreases as the inverse square of this detuning. Compared to other line shapes, like the Gaussian we'll soon study, this is indeed a slow decay. This means that even far from the line center, a Lorentzian line can still have a non-negligible intensity. These are often called "heavy tails" or "far wings."

The final bullet point provides a crucial piece of context for why we need to study other broadening mechanisms: "**Unfortunately, in gases the Lorentzian is rarely seen directly because larger effects obscure it.**"

While natural broadening is always present, in many practical situations, especially in gases at non-cryogenic temperatures, other broadening mechanisms are much more significant and effectively mask the underlying natural Lorentzian profile, particularly near the line center. The most prominent of these in low-pressure gases is often Doppler broadening, which we are about to discuss. In higher pressure gases, collisional broadening, which also results in a Lorentzian profile, can become dominant. But the purely *natural* Lorentzian is often much narrower than these other contributions.

This sets the stage perfectly for introducing the Doppler effect.

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Now we **Enter Thermal Motion – The Doppler Problem**. This is where we start to build our understanding of Doppler broadening, which is a type of *inhomogeneous* broadening, meaning it arises because different atoms in the ensemble experience slightly different conditions – in this case, different velocities.

The first bullet point sets the scene: "Gas molecules at temperature T move randomly; each molecule constitutes a moving source or absorber." In any gas sample above absolute zero, the constituent atoms or molecules are in constant, chaotic thermal motion. They are moving in all directions with a range of speeds, described by a statistical distribution like the Maxwell-Boltzmann distribution. When an atom or molecule emits or absorbs light, if it's moving, it acts as a moving source (for emission) or a moving absorber/observer (for absorption).

The second point is key: "Motion along observer's line of sight **shifts the apparent frequency** via the Doppler effect." You're all familiar with the Doppler effect from sound waves – the pitch of an ambulance siren changes as it moves towards you and then away from you. A similar effect occurs with light waves. If a light-emitting atom is moving towards an observer (say, a detector), the observed frequency of the light will be higher (blue-shifted) than the frequency emitted in the atom's own rest frame. If it's moving away, the observed frequency will be lower (red-shifted). Crucially, it's the component of the velocity *along the line of sight* between the atom and the observer that matters for this frequency shift. Motion perpendicular to the line of sight produces a much smaller, second-order effect (the transverse Doppler effect), which we usually neglect in this context.

Finally, "Shift adds or subtracts from ω_0 (omega naught) depending on velocity component v_z (v sub z)." Let's define ω_0 as the intrinsic, unshifted angular frequency of the transition (what you'd observe if the atom were at rest). If we define our z-axis as the line of sight, then v_z is the component of the molecule's velocity along this axis. If v_z is positive (moving towards the observer, if the observer is at positive z, or if light propagates along $+z$ and the atom moves along $-z$ for absorption), the frequency increases. If v_z is negative, the frequency decreases. We'll quantify this shift shortly.

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This leads us directly to the concept of **Doppler broadening**: "ensemble of many differently-moving molecules ⇒ distribution of shifted frequencies ⇒ overall line broadening."

Let's unpack this. We're not looking at a single atom; we're observing a huge number of them, an ensemble. As we just discussed, each atom, due to its thermal motion, will have some velocity component v_z along our line of sight. The Maxwell-Boltzmann distribution tells us that these v_z values will be spread out – some atoms moving towards us slowly, some quickly, some away from us slowly, some quickly, and many with very small v_z.

Since each unique value of v_z leads to a slightly different Doppler-shifted frequency, the collection of all these slightly different frequencies from all the atoms in the ensemble effectively "smears out" the spectral line. What would have been a single frequency ω_0 (if all atoms were at rest and ignoring natural broadening for a moment) now becomes a band of frequencies.

This is the essence of Doppler broadening. It's an *inhomogeneous* broadening mechanism because each atom contributes to the line at a frequency determined by its *individual* velocity. The overall line shape we observe is the sum, or integral, of all these individual, shifted contributions, weighted by the probability of each velocity occurring. This results in an "overall line broadening." We will see that this typically leads to a Gaussian line shape.

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This slide provides a wonderful visual illustration of the **Doppler Effect: Molecular Motion and Frequency Shift.**

Let's look at the three scenarios depicted, all relative to a detector shown on the right. The dashed horizontal line in the middle two scenarios represents the line of sight, which we can call the z-axis. The wavy lines represent the light waves emitted by the molecule (the grey circle).

* **Top Scenario: Molecule moving away.** The molecule has a velocity component $-v_{\text{z}}$ (minus v_{z}), meaning it's moving to the left, away from the detector. The emitted wave, shown in red, is stretched out. Its wavelength is longer, and therefore its frequency ω (omega) is less than ω_0 (omega naught, the rest-frame frequency). This is a **Red Shift**. The wave crests are emitted further apart in space from the perspective of the detector because the molecule recedes between emitting successive crests.

* **Middle Scenario: Molecule moving perpendicular.** Here, the velocity component along the line of sight, v_{z}, is 0. The molecule is moving upwards, perpendicular to the z-axis. The emitted wave, shown in green, has a frequency ω approximately equal to ω_0. There is **No Shift** (or, more precisely, only the very small transverse Doppler effect, which we are

ignoring). The spacing of the wave crests along the z-axis is essentially unchanged from the rest frame emission.

* **Bottom Scenario: Molecule moving towards.** The molecule has a velocity component $+v_z$ (plus v_z), moving to the right, towards the detector. The emitted wave, shown in blue, is compressed. Its wavelength is shorter, and its frequency ω is greater than ω_0. This is a **Blue Shift**. The wave crests are emitted closer together in space from the detector's viewpoint because the molecule advances between emitting successive crests.

This diagram beautifully captures the core idea: the velocity component along the line of sight directly influences the observed wavelength and frequency. An ensemble of molecules will have a statistical distribution of these v_z values, leading to a distribution of observed frequencies.

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Now, let's formalize the **Geometry & Notation for Doppler Shift**. Establishing a clear coordinate system and consistent notation is crucial for the derivations that follow.

First bullet: "Choose laboratory z-axis along propagation direction of light." This is a standard and convenient choice. So, light is traveling, say, in the positive z direction. If we are considering emission, the detector would be at some large positive z. If we are considering absorption of this light beam by molecules, the molecules will be interacting with this z-propagating light.

Second bullet: "Wave vector $\mathbf{k} = (0,0,k_z)$." The wave vector $\mathbf{k}$ points in the direction of wave propagation and its magnitude is related to the wavelength and frequency. Since the light propagates along the z-axis, the x and y components of $\mathbf{k}$ are zero. So, $\mathbf{k}$ is a vector with components $(0,0,k_z)$, where k_z is the magnitude of $\mathbf{k}$ along the z-axis.

Third bullet: "Magnitude $k_z = \frac{2\pi}{\lambda} = \frac{\omega}{c}$ (k sub zed equals two pi over lambda equals omega over c)." The magnitude of the wave vector, k (which is k_z in our case since it's along z), is $\frac{2\pi}{\lambda}$ divided by the wavelength λ. It's also equal to the angular frequency ω divided by the speed of light, c. These are standard relations for electromagnetic waves.

Fourth bullet: "Molecular velocity $\mathbf{v} = (v_\text{x}, v_\text{y}, v_\text{z})$ (vector v equals v sub x, v sub y, v sub z)." Each molecule in our gas sample has a velocity vector $\mathbf{v}$, which can have components in all three directions. v_x and v_y are the velocity components perpendicular to the light propagation, and v_z is the component parallel (or anti-parallel) to the light propagation.

Fifth bullet: "Component relevant for shift is v_z because $\mathbf{k} \cdot \mathbf{v} = k_\text{z} v_\text{z}$ (k dot v equals k sub zed times v sub zed)." As we mentioned, the Doppler shift depends on the component of the molecular velocity along the direction of the wave vector $\mathbf{k}$. This is mathematically captured by the dot product $\mathbf{k} \cdot \mathbf{v}$. Since our $\mathbf{k}$ is $(0,0,k_\text{z})$ and $\mathbf{v}$ is $(v_\text{x}, v_\text{y}, v_\text{z})$, their dot product is $(0 \cdot v_\text{x}) + (0 \cdot v_\text{y}) + (k_\text{z} \cdot v_\text{z})$, which simplifies to $k_\text{z} v_\text{z}$. This confirms that only the v_z component of the molecular velocity, the one along the line of sight, contributes to the (first-order) Doppler shift.

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Continuing with our setup, a very important approximation is stated here: "We treat speeds $|v_\text{z}| \ll c$ (absolute value of v_z is much, much less than c) → use **linear Doppler approximation** (relativistic corrections deferred)."

This is a crucial simplification that is valid for most atoms and molecules in typical laser spectroscopy experiments. The speeds of atoms or molecules due to thermal motion, even at thousands of Kelvin, are typically many orders of magnitude smaller than the speed of light, c (which is approximately 3×10^8 meters per second). For example, for a nitrogen molecule at room temperature, the root-mean-square speed is about 500 meters per second, which is about $1.7 \times 10^{-6}\,c$. So, the ratio $\frac{v_\text{z}}{c}$ is very small.

When $\frac{v}{c}$ is small, the full relativistic Doppler formula can be accurately approximated by its first-order term, which is linear in $\frac{v_z}{c}$. This is what we call the linear Doppler approximation. We are deferring, or neglecting, the higher-order terms which include relativistic effects like time dilation (the transverse Doppler effect is one such relativistic effect, proportional to $\left(\frac{v}{c}\right)^2$). These relativistic corrections are usually tiny and only become important in very high-precision measurements or for particles moving at near-relativistic speeds, neither of which is typically the case in standard gas-phase laser spectroscopy. So, for our purposes, the linear approximation is excellent.

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Now let's apply this to a specific scenario: **Doppler Shift for Spontaneous Emission**.

* First bullet: "Consider a molecule that has just decayed and emitted a photon." So, we have an excited molecule, it transitions to a lower energy state, and in doing so, releases a photon.

* Second bullet: "In molecule's rest frame: photon angular frequency ω_0 (omega naught)." If we were sitting on the molecule, moving with it, we would measure the emitted photon's angular frequency to be ω_0. This ω_0 is determined by the energy difference between the two quantum states involved in the transition,

$$\omega_0 = \frac{E_{\text{upper}} - E_{\text{lower}}}{\hbar}.$$

This is the "true" or "unshifted" frequency.

* Third bullet: "For a laboratory observer:" This is where the Doppler effect comes in. An observer in the lab frame, relative to whom the molecule is moving with velocity $\mathbf{v}$ (and thus velocity component v_z along the line of sight to the observer, assuming light travels along z), will measure a

different frequency, ω_e (omega sub e, for emitted frequency). The formula for this observed frequency in the linear Doppler approximation is:

$$\omega_\text{e} = \omega_0 + \mathbf{k} \cdot \mathbf{v}$$

And using our established geometry where $\mathbf{k}$ is along the z-axis with magnitude k_z, and only v_z contributes, this becomes:

$$\omega_\text{e} = \omega_0 + k_\text{z} v_\text{z}.$$

Let's quickly see where this comes from. The shift $\Delta\omega = \omega_\text{e} - \omega_0$ is given by $\omega_0 \frac{v_\text{z}}{c}$ when the source moves towards the observer with speed v_z. Since $k_\text{z} = \frac{\omega}{c} \approx \frac{\omega_0}{c}$ (because the shift is small), we can write $k_\text{z} v_\text{z} \approx \frac{\omega_0}{c} v_\text{z}$. So,

$$\omega_\text{e} = \omega_0 \left(1 + \frac{v_\text{z}}{c}\right) = \omega_0 + \omega_0 \left(\frac{v_\text{z}}{c}\right),$$

which is $\omega_0 + k_\text{z} v_\text{z}$. This formula shows that the observed frequency ω_e is the rest frequency ω_0 plus a shift term $k_\text{z} v_\text{z}$.

* Fourth bullet: "v_z > 0: molecule moves toward observer ⇒ ω_e > ω_0 (blue shift)." If $v_\text{z} > 0$ (meaning the molecule is moving towards the observer, or more generally, the velocity component is in the same direction as $\mathbf{k}$ if $\mathbf{k}$ points from source to observer), then $k_\text{z} v_\text{z}$ is a positive term, so ω_e will be greater than ω_0. This is a higher frequency, shorter wavelength, hence a "blue shift."

* Fifth bullet: "v_z < 0: molecule recedes ⇒ ω_e < ω_0 (red shift)." Conversely, if $v_\text{z} < 0$ (molecule moving away from the observer, or velocity component opposite to $\mathbf{k}$), then $k_\text{z} v_\text{z}$ is negative, making ω_e less than ω_0. This is a lower frequency, longer wavelength, hence a "red shift."

This clearly establishes the linear relationship between the velocity component v_z and the observed frequency shift for spontaneously emitted light.

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This slide concisely states a critical consequence of the relationship we just established:

"**Each value of** v_z (v sub zed) thus maps to a unique emission frequency."

Given our formula from the previous page, $\omega_e = \omega_0 + k_z v_z$, for a fixed rest frequency ω_0 and a fixed wave vector magnitude k_z (which is essentially $\frac{\omega_0}{c}$), there is a direct, linear correspondence between the velocity component v_z of the emitting molecule along the line of sight and the frequency ω_e observed in the laboratory.

If you tell me the v_z of a specific molecule, I can tell you the exact frequency at which the lab observer will detect its emitted photon. Conversely, if I measure a specific emission frequency ω_e, I can (in principle, if I know ω_0) infer the v_z of the molecule that emitted it.

This one-to-one mapping is the fundamental reason why a distribution of velocities (like the Maxwell-Boltzmann distribution for v_z in a thermal gas) will directly translate into a distribution of observed emission frequencies, thereby creating the Doppler-broadened spectral line. We are essentially using the Doppler effect to perform a kind of velocity-to-frequency conversion.

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Here we have a graph illustrating the **Doppler Shift: Observed Frequency** ω_e vs. Velocity Component v_z. This visually represents the linear mapping we just discussed.

Let's examine the graph:

- The vertical axis represents the observed angular frequency, ω_e.
- The horizontal axis represents the velocity component of the molecule along the line of sight, v_z.

- The central point on the vertical axis is ω_0, the rest-frame frequency. This corresponds to $v_\text{z} = 0$ on the horizontal axis, as indicated by the red dot at $(0, \omega_0)$. If a molecule has no velocity component along the line of sight, its emitted frequency is unshifted.

The relationship is plotted as a straight blue line passing through $(0, \omega_0)$ with a positive slope. The equation of this line is shown as:

$$\omega_\text{e} = \omega_0 + k_\text{z} v_\text{z}$$

where k_z (which is $\frac{\omega_0}{c}$) is the slope of this line.

The graph is divided into two regions:

- **To the left of the vertical axis (**$v_\text{z} < 0$): This region is shaded light red and labeled "Red Shift ($\omega_\text{e} < \omega_0$, $v_\text{z} < 0$)". Here, molecules are moving away from the observer (or in the direction opposite to light propagation considered for k_z), so their v_z is negative. Consequently, the observed frequency ω_e is less than ω_0. The line extends down to some $-v_{max}$ on the velocity axis, corresponding to the lowest observed frequencies.

- **To the right of the vertical axis (**$v_\text{z} > 0$): This region is shaded light blue and labeled "Blue Shift ($\omega_\text{e} > \omega_0$, $v_\text{z} > 0$)". Here, molecules are moving towards the observer, their v_z is positive, and the observed frequency ω_e is greater than ω_0. The line extends up to some $+v_{max}$ on the velocity axis, corresponding to the highest observed frequencies.

This graph powerfully illustrates that the range of velocities present in the gas (from $-v_{max}$ to $+v_{max}$, though in reality it's a continuous distribution) will directly map to a range of observed frequencies centered around ω_0. The wider the spread of v_z values, the wider the spread of ω_e values, and thus the broader the spectral line.

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Now let's switch gears slightly and consider the **Doppler Shift for Absorption**. The physics is very similar, but the perspective is a bit different.

* First bullet: "Incident monochromatic plane wave in lab:" We imagine we are shining a laser beam, which we can approximate as a monochromatic (single-frequency) plane wave, through our gas sample. The electric field of this wave in the laboratory frame is given by:

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 \exp\big(i(\omega t - \mathbf{k}\cdot\mathbf{r})\big)$$

* Second bullet: "In molecule's co-moving frame (velocity $\mathbf{v}$): time and space transform so that the **observed angular frequency becomes** $\omega' = \omega - \mathbf{k}\cdot\mathbf{v}$."

Now, consider a molecule moving with velocity $\mathbf{v}$ relative to the lab. From the molecule's perspective (its co-moving frame), this incident lab-frequency ω light will appear to have a different frequency, which we call ω'. This transformation is a result of the Doppler effect. The formula $\omega' = \omega - \mathbf{k}\cdot\mathbf{v}$ arises from how the phase of the wave ($\omega t - \mathbf{k}\cdot\mathbf{r}$) transforms between the lab frame and the molecule's moving frame. Specifically, if t' and $\mathbf{r}'$ are time and position in the molecule's frame, and t, $\mathbf{r}$ are in the lab frame, the phase must be invariant:

$$\omega t - \mathbf{k}\cdot\mathbf{r} = \omega' t' - \mathbf{k}'\cdot\mathbf{r}'$$

Using Galilean transformations for non-relativistic speeds ($\mathbf{r} = \mathbf{r}' + \mathbf{v}t,\ t = t'$), one can derive this relationship for the frequency. Notice the sign difference compared to the emission case $\omega_{\text{e}} = \omega_0 + \mathbf{k}\cdot\mathbf{v}$. Here, ω is the lab frequency and ω' is the frequency *seen by the molecule*.

* Third bullet: "Absorption occurs only when internal resonance condition met: $\omega' = \omega_0$."

A molecule will only absorb the incident light if the frequency it *perceives* in its own rest frame, ω', matches its natural resonant absorption frequency,

ω_0. This ω_0 is the same intrinsic transition frequency we discussed for emission, determined by the molecule's internal energy level structure.

So, for absorption to happen, the lab frequency ω, the molecular velocity $\mathbf{v}$, and the rest-frame resonance ω_0 must satisfy

$$\omega - \mathbf{k} \cdot \mathbf{v} = \omega_0.$$

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Continuing with the absorption case, we want to find the laboratory frequency ω that will be absorbed by a molecule moving with velocity $\mathbf{v}$.

- First bullet: "Solve for laboratory frequency ω:" From the previous slide, the condition for absorption is $\omega' = \omega_0$, and $\omega' = \omega - \mathbf{k} \cdot \mathbf{v}$. Substituting $\omega' = \omega_0$, we get $\omega_0 = \omega - \mathbf{k} \cdot \mathbf{v}$. Solving this for ω, the lab frequency that gets absorbed (let's call it ω_a for absorbed frequency), gives:

$$\omega_\mathrm{a} = \omega_0 + \mathbf{k} \cdot \mathbf{v}$$

- Second bullet: "Same linear dependence as emission case." Compare this $\omega_\mathrm{a} = \omega_0 + \mathbf{k} \cdot \mathbf{v}$ with the formula for the observed frequency in emission, which was $\omega_\mathrm{e} = \omega_0 + \mathbf{k} \cdot \mathbf{v}$. They are mathematically identical! This is a very important result. The relationship between the lab frequency involved in the resonant interaction and the molecule's velocity is the same whether we are considering emission from a moving molecule or absorption by a moving molecule of lab-fixed radiation.

- Third bullet: "Explicit for chosen geometry $\mathbf{k} = (0,0,k_\mathrm{z})$:" If we again assume our light propagates along the z-axis, so $\mathbf{k} = (0,0,k_\mathrm{z})$ and $\mathbf{k} \cdot \mathbf{v} = k_\mathrm{z} v_\mathrm{z}$, the equation becomes:

$$\omega_\mathrm{a} = \omega_0 + k_\mathrm{z} v_\mathrm{z}$$

And if we further substitute $k_\mathrm{z} = \omega / c$ (where ω is the lab frequency, so ω_a here) and make the common approximation that in the term $k_\mathrm{z} v_\mathrm{z}$, we can approximate ω_a with ω_0 (since v_z/c is small, the shift $k_\text{z}v_\text{z}$ is much smaller than ω_0), then $k_\text{z} \approx \omega_0/c$.

So, $\omega_\text{a} \approx \omega_0 + (\omega_0/c)v_\text{z}$.

This can be rewritten as:

$$\omega_\text{a} = \omega_0\left(1 + \frac{v_\text{z}}{c}\right)$$

This is the lab frequency that a molecule moving with velocity component v_z along the light propagation direction will absorb, given its rest-frame absorption frequency is ω_0. A molecule moving towards an oncoming light beam ($v_\text{z} < 0$ if light is in $+z$ direction, or more generally if $\mathbf{v}$ is anti-parallel to $\mathbf{k}$) will absorb a lab frequency ω_a that is *lower* than ω_0, because in its frame, this lower lab frequency gets blue-shifted up to ω_0. Conversely, a molecule moving away from the light source ($v_\text{z} > 0$, or $\mathbf{v}$ parallel to $\mathbf{k}$) will absorb a lab frequency ω_a that is *higher* than ω_0, because in its frame, this higher lab frequency gets red-shifted down to ω_0.

This symmetry between emission and absorption is very convenient.

Page 17:

Now, let's briefly discuss the **Validity & Higher-Order Doppler Effects**. We've been relying on the linear Doppler approximation. How good is it, and what happens when it's not sufficient?

* First bullet: "Linear approximation adequate until $\frac{|v_\text{z}|}{c} \approx 10^{-5}$ (order of 10^{-5})." As we mentioned, thermal speeds are typically $\frac{v}{c}$ of 10^{-6} to 10^{-7}. So, 10^{-5} is still well within the regime where the linear approximation is usually excellent. To reach $\frac{v}{c} \approx 10^{-5}$, you'd need either very light particles or very high temperatures, or you'd be looking at astrophysical objects with significant bulk velocities. For most lab-based atomic and molecular spectroscopy, $\left(\frac{v}{c}\right)^2$ terms are negligible compared to $\frac{v}{c}$ terms.

* Second bullet: "**Quadratic/relativistic Doppler** adds terms $\propto \left(\frac{v}{c}\right)^2$ (proportional to $\frac{v}{c}$ over c^2)." The next level of correction to the Doppler formula involves terms that go as the square of the velocity divided by the speed of light squared. These arise from special relativity, primarily from the time dilation effect. A moving clock (like the oscillating internal structure of an atom) runs slower as observed from the lab frame by a factor of

$$\gamma_{\text{rel}} = \frac{1}{\sqrt{1-\left(\frac{v}{c}\right)^2}}.$$

When $\frac{v}{c}$ is small, this γ_{rel} can be expanded as

$$1+\frac{1}{2}\left(\frac{v}{c}\right)^2+\cdots$$

which introduces terms of order $\left(\frac{v}{c}\right)^2$. This leads to what's called the transverse Doppler effect (if motion is purely perpendicular to observation) and also modifies the longitudinal Doppler effect.

* Third bullet: "Important in precision metrology (atomic clocks, Mössbauer spectroscopy)." While often negligible, these $\left(\frac{v}{c}\right)^2$ terms are not *always* negligible. In ultra-high precision measurements, such as those aiming to define frequency standards with atomic clocks, or in Mössbauer spectroscopy where nuclear transitions have incredibly narrow natural linewidths, these second-order Doppler shifts can become significant and must be accounted for. Atomic clocks often use ion traps to cool and confine ions, minimizing v and thus these shifts.

* Fourth bullet: "For the temperatures and masses addressed here (hundreds of kelvin, atomic masses), linear term dominates." This is a reassurance. For the typical conditions we encounter in this course – gases at temperatures from cryogenic up to a few thousand Kelvin, involving

atoms and molecules with typical atomic masses – the linear Doppler effect ($\propto \frac{v}{c}$) is by far the dominant source of frequency shift due to motion. The quadratic terms are usually orders of magnitude smaller. So, our focus on the linear Doppler effect is well justified for deriving the primary Doppler broadening line shape.

Page 18:

To quantify Doppler broadening, we need to know how molecular velocities are distributed. This brings us to the **Maxwell-Boltzmann Velocity Distribution**.

* First bullet: "At equilibrium the **probability density** for the z-component of velocity is".

In a gas in thermal equilibrium at a temperature T, the velocities of the molecules are not all the same; they follow a statistical distribution. Since the Doppler shift depends on v_z (the velocity component along the line of sight, our chosen z-axis), we are particularly interested in the distribution of v_z. The Maxwell-Boltzmann distribution gives us this. The probability density function for v_z, denoted $f(v_\mathrm{z})$, is given by:

$$f(v_\mathrm{z}) = \frac{1}{v_\mathrm{p}\sqrt{\pi}} \exp\left[-\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2\right]$$

(f of v sub zed equals, in square brackets, one over the product of v sub p and the square root of pi, all times the exponential of, in square brackets, minus the square of the ratio v sub zed over v sub p).

Let's understand the terms: * $f(v_\mathrm{z})$ is a probability density function. This means that $f(v_\mathrm{z})\,dv_\mathrm{z}$ gives the probability that a molecule will have its z-component of velocity between v_z and $v_\mathrm{z} + dv_\mathrm{z}$. * The term $\exp\left[-\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2\right]$ is a Gaussian function. It shows that the distribution is symmetric around $v_\mathrm{z} = 0$ (most probable v_z is zero) and falls off rapidly for larger positive or negative v_z. * v_p is a characteristic speed, called the most probable speed component magnitude, which sets the scale for the width of this Gaussian distribution. * The prefactor $\frac{1}{v_p\sqrt{\pi}}$ is a normalization constant, ensuring that if we integrate $f(v_z)\,dv_z$ from $v_z = -\infty$ to $+\infty$, the total probability is 1.

* Second bullet defines v_p:

$$v_p = \sqrt{\frac{2\,kT}{m}}$$

(v sub p equals the square root of 2 k T over m).

Here: * k is the Boltzmann constant. * T is the absolute temperature in Kelvin. * m is the mass of a single molecule in kilograms. So, v_p increases with temperature (hotter gas, wider velocity distribution) and decreases with molecular mass (heavier molecules are more sluggish at a given temperature).

* Third bullet gives the value of the Boltzmann constant:

$$k = 1.380649 \times 10^{-23}\ \mathrm{J\ K^{-1}}$$

(Joules per Kelvin).

This Maxwell-Boltzmann distribution for v_z is the starting point for deriving the Doppler line shape. Since each v_z maps to a specific frequency shift, this Gaussian distribution of velocities will directly lead to a Gaussian distribution of observed frequencies.

Page 19:

Continuing with the Maxwell-Boltzmann distribution context:

First, a reminder: " m – molecular mass (kg)." It's crucial to use consistent units in the formula for v_p, so mass should be in kilograms if k is in J/K and T in Kelvin, to get v_p in m/s.

Second bullet: "Number density of level i:

$$N_\mathrm{i} = \int_{-\infty}^{+\infty} n_\mathrm{i}\,(v_\mathrm{z})\,dv_\mathrm{z}$$

(Capital N_i equals the integral from minus infinity to plus infinity of $n_\mathrm{i}(v_\mathrm{z})\,dv_\mathrm{z}$). This equation defines N_i, the total number of molecules per unit volume (number density) that are in a specific quantum state 'i' (e.g., the lower state of an absorbing transition).

The term $n_\mathrm{i}(v_\mathrm{z})\,dv_\mathrm{z}$ represents the number density of molecules that are in state i *and* have their z-component of velocity in the small range between v_z and $v_\mathrm{z} + dv_\mathrm{z}$.

So, $n_\mathrm{i}(v_\mathrm{z})$ is the velocity distribution function for particles in state i.

If the gas is in thermal equilibrium, we can relate $n_\mathrm{i}(v_\mathrm{z})$ to the total number density N_i and the normalized Maxwell-Boltzmann probability density $f(v_\mathrm{z})$ we saw on the previous page:

$$n_\mathrm{i}(v_\mathrm{z}) = N_\mathrm{i}\,f(v_\mathrm{z})$$

where

$$f(v_\mathrm{z}) = \frac{1}{v_\mathrm{p}\sqrt{\pi}}\exp\left[-\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2\right].$$

So, $n_\mathrm{i}(v_\mathrm{z})\,dv_\mathrm{z}$ is the number of molecules per unit volume in state i that are "in the velocity bin" dv_z around v_z. Summing (integrating) these over all possible v_z gives the total number density N_i of molecules in that state.

This framework allows us to count how many molecules have the right velocity v_z to interact with light of a particular frequency ω.

Page 20

This slide provides a graphical representation of the **Maxwell-Boltzmann Velocity Distribution** for the $f(v_\mathrm{z})$ for the z-component of velocity, though the vertical axis isn't explicitly labeled $f(v_\mathrm{z})$. Let's assume the horizontal axis is scaled by v_p, so it represents $x = \frac{v_\mathrm{z}}{v_\mathrm{p}}$. Then the function plotted is proportional to $\exp(-x^2)$, and if it's normalized as $f(x) = \frac{1}{\sqrt{\pi}} \exp(-x^2)$, the peak value (at $x = 0$) is $\frac{1}{\sqrt{\pi}}$.

Let's interpret the features of this bell-shaped curve:

* The curve is perfectly symmetric and centered at $\frac{v_\mathrm{z}}{v_\mathrm{p}} = 0$, which means the most probable z-component of velocity is zero. Equal numbers of molecules are moving in the $+z$ and $-z$ directions at any given speed.

* The peak height is labeled as "$\frac{1}{\sqrt{\pi}}$" (one over square root of pi). This corresponds to $f(v_\mathrm{z} = 0) \times v_\mathrm{p}$, or $f(x = 0)$ if $x = \frac{v_\mathrm{z}}{v_\mathrm{p}}$. Given that v_p has units of speed, and $f(v_\mathrm{z})$ has units of inverse speed, plotting $\frac{1}{\sqrt{\pi}}$ suggests the x-axis is indeed the dimensionless $\frac{v_\mathrm{z}}{v_\mathrm{p}}$.

* The **Full Width at Half Maximum (FWHM)** is indicated. The intensity drops to half its peak value when

$$\exp\left(-\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2\right) = \frac{1}{2}.$$

This means

$$-\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2 = \ln\left(\frac{1}{2}\right) = -\ln(2).$$

So, $\left(\frac{v_\mathrm{z}}{v_\mathrm{p}}\right)^2 = \ln(2)$, which gives $\frac{v_\mathrm{z}}{v_\mathrm{p}} = \pm\sqrt{\ln 2}$ (plus or minus square root of natural log of 2).

The FWHM is the difference between these two points:

$$\sqrt{\ln 2} - \left(-\sqrt{\ln 2}\right) = 2\sqrt{\ln 2}.$$

The value of $\sqrt{\ln 2}$ is approximately $\sqrt{0.693} \approx 0.832$. So the FWHM is about 1.665 in units of $\frac{v_\mathrm{z}}{v_\mathrm{p}}$. The graph correctly labels the FWHM as "FWHM = $2\sqrt{\ln 2}$". The half-max points on the x-axis are labeled $-\sqrt{\ln 2}$ and $+\sqrt{\ln 2}$. The height at these points is labeled "$\frac{1}{2\sqrt{\pi}}$", which is half of the peak height $\frac{1}{\sqrt{\pi}}$.

* Another point of interest is when $\frac{v_\mathrm{z}}{v_\mathrm{p}} = \pm 1$. At these points, the value of the Gaussian is $\frac{1}{\sqrt{\pi}} e^{-1}$ (one over root pi, times e^{-1}), as labeled. This corresponds to the $\frac{1}{e}$ width points of the distribution if we were looking at the exponential term alone.

This graph reinforces the Gaussian nature of the v_z distribution. It's this very shape that will be translated into the frequency domain to give the Doppler-broadened spectral line profile.

Page 21:

Now we come to a crucial step: **Linking Velocity to Frequency**. We need to formally connect the velocity distribution $f(v_\mathrm{z})$ to a frequency distribution $I(\omega)$.

First bullet: "Relationship $v_\mathrm{z} \leftrightarrow \omega$ from absorption formula:"

Recall from page 16, the lab frequency ω_a (which we'll just call ω now) that a molecule with rest frequency ω_0 and velocity component v_z absorbs is given by $\omega \approx \omega_0 \left(1 + \frac{v_\mathrm{z}}{c}\right)$. We can rearrange this to solve for v_z: $\frac{\omega}{\omega_0} = 1 + \frac{v_\mathrm{z}}{c}$ $\frac{v_\mathrm{z}}{c} = \frac{\omega}{\omega_0} - 1 = \frac{\omega - \omega_0}{\omega_0}$ So, $v_\mathrm{z} = c \cdot \frac{\omega - \omega_0}{\omega_0}$ This equation explicitly gives the z-component of velocity, v_z, of a molecule that is resonant with incident light of frequency ω, given its rest-frame resonance is ω_0. This confirms our earlier statement of a direct mapping.

Second bullet: "Infinitesimal transformation:"

To transform a probability distribution from one variable (v_z) to another (ω), we need the relationship between their differentials, dv_z and $d\omega$. We get this by differentiating the expression for v_z with respect to ω (treating c and ω_0 as constants): $dv_\text{z} = \frac{d}{d\omega}\left[c \cdot \frac{\omega-\omega_0}{\omega_0}\right] d\omega$ $dv_\text{z} = \left[\frac{c}{\omega_0} \cdot \frac{d}{d\omega}(\omega - \omega_0)\right] d\omega$ $dv_\text{z} = \left[\frac{c}{\omega_0} \cdot (1 - 0)\right] d\omega$ So, $dv_\text{z} = \frac{c}{\omega_0} d\omega$ This tells us how a small interval of velocities, dv_z, corresponds to a small interval of frequencies, $d\omega$. The term $\frac{c}{\omega_0}$ is the Jacobian of the transformation, or rather its inverse here ($\frac{d\omega}{dv_\text{z}} = \frac{\omega_0}{c}$). The absolute value of $\frac{dv_\text{z}}{d\omega}$ is $\frac{c}{\omega_0}$.

These two equations are the tools we need to convert the Maxwell-Boltzmann velocity distribution $f(v_\text{z})$ into a spectral line shape $I(\omega)$.

Page 22:

Let's continue with the implications of linking velocity to frequency.

* The first bullet point here summarizes the next step in our derivation: "**Substitute into velocity distribution to obtain frequency distribution of resonant molecules.**"

The idea is as follows: The number of molecules $dN(v_\text{z})$ having their z-velocity component between v_z and $v_\text{z} + dv_\text{z}$ is given by \(N_\text{total} *f(v_\text{z}) dv_\text{z}\), where* $f(v_\text{z})$ is the Maxwell-Boltzmann distribution. Since each v_z corresponds to a unique resonant frequency ω (via $v_\text{z} = c(\omega - \omega_0)/\omega_0$), the molecules in this velocity interval dv_z are precisely those molecules that are resonant with light in the corresponding frequency interval $d\omega$ (where $d\omega = (\omega_0/c)dv_\text{z}$). So, the number of molecules $dN(\omega)$ resonant in the frequency interval $d\omega$ around ω will be proportional to \(N_\text{total} f(v_\text{z}(\omega)) *

\left|\frac{dv_\text{z}}{d\omega}\right| d\omega\). We've found $v_\text{z}(\omega)$ and $\left|\frac{dv_\text{z}}{d\omega}\right|$, so we can perform this substitution.

* The second bullet point re-emphasizes this connection: "**Each** ω interval collects molecules whose v_z satisfy the above relation."

When we probe the gas with light of a specific frequency ω (or a narrow band $d\omega$ around ω), we are selectively interacting only with that sub-population of molecules whose v_z values are such that they are Doppler-shifted into resonance with ω. Molecules with other v_z values will be resonant at other frequencies and will not interact with our light at frequency ω. Therefore, the intensity of absorption (or emission) at frequency ω will be directly proportional to the number of molecules that happen to have the "correct" v_z to be resonant at ω. This is the heart of how the velocity distribution shapes the spectral line.

Page 23:

Now we arrive at the **Derivation of Gaussian Intensity Profile**, which is the culmination of our discussion on Doppler broadening.

* First bullet: "Count of resonant molecules within $(\omega, \omega + d\omega)$:"

Let $n_\text{i}(\omega)d\omega$ be the number density of molecules in state 'i' that are resonant with light in the frequency interval from ω to $\omega + d\omega$. This is obtained by taking the Maxwell-Boltzmann distribution for v_z, substituting v_z in terms of ω, and multiplying by the Jacobian of the transformation $\left|\frac{dv_\text{z}}{d\omega}\right|$.

Recall:

$$f(v_\text{z}) = \frac{1}{v_\text{p}\sqrt{\pi}} \exp\left[-\left(\frac{v_\text{z}}{v_\text{p}}\right)^2\right]$$

$$v_\text{z} = c\,\frac{\omega - \omega_0}{\omega_0}$$

$dv_\mathrm{z} = \frac{c}{\omega_0} d\omega$, so $\left|\frac{dv_\mathrm{z}}{d\omega}\right| = \frac{c}{\omega_0}$.

If N_i is the total number density of molecules in state i, then the number density in $d\omega$ is:

$$n_\mathrm{i}(\omega) d\omega = N_\mathrm{i} \cdot f\big(v_\mathrm{z}(\omega)\big) \cdot \left|\frac{dv_\mathrm{z}}{d\omega}\right| d\omega$$

$$n_\mathrm{i}(\omega) d\omega = N_\mathrm{i} \cdot \frac{1}{v_\mathrm{p}\sqrt{\pi}} \cdot \exp\left[-\left(\frac{\frac{c(\omega - \omega_0)}{\omega_0}}{v_\mathrm{p}}\right)^2\right] \cdot \frac{c}{\omega_0} d\omega$$

Rearranging the terms in the prefactor, we get:

$$n_\mathrm{i}(\omega) d\omega = N_\mathrm{i} \cdot \frac{c}{\omega_0 v_\mathrm{p}\sqrt{\pi}} \exp\left[-\left(\frac{c(\omega - \omega_0)}{\omega_0 v_\mathrm{p}}\right)^2\right] d\omega$$

This is exactly the formula shown on the slide for $n_\mathrm{i}(\omega) d\omega$, the number of resonant molecules. This expression gives us the distribution of resonant molecules as a function of frequency ω. Notice the exponential term: it's a Gaussian function of ω, centered at ω_0, and its width is determined by the term $\frac{\omega_0 v_\mathrm{p}}{c}$.

* Second bullet: "Emitted/absorbed power $P(\omega) \propto n_\mathrm{i}(\omega) \Rightarrow$ same functional form for intensity:"

The power emitted or absorbed by the gas at a frequency ω is directly proportional to the number of molecules $n_\mathrm{i}(\omega)$ that are resonant at that frequency (assuming non-saturated conditions). Therefore, the spectral intensity profile, $I(\omega)$, will have the same functional form as $n_\mathrm{i}(\omega)$.

So, we can write the intensity $I(\omega)$ as:

$$I(\omega) = I_0 \exp\left[-\left(\frac{c(\omega - \omega_0)}{\omega_0 v_\mathrm{p}}\right)^2\right]$$

Here, I_0 (capital I sub zero) is the peak intensity, which occurs at $\omega = \omega_0$ (when the exponential term is 1). I_0 incorporates the pre-exponential factor from $n_\mathrm{i}(\omega)$ and other proportionality constants related to the strength of the transition.

This equation explicitly shows that the Doppler-broadened line shape is a Gaussian function of frequency.

Page 24:

This slide simply states the conclusion from our derivation: "**We have derived a Gaussian line shape (also called "normal" distribution).**"

Indeed, the expression $I(\omega) = I_0 \cdot \exp\left[-\left(\frac{c(\omega-\omega_0)}{\omega_0\, v_\mathrm{p}}\right)^2\right]$ is the mathematical form of a Gaussian function, centered at ω_0, with a characteristic width determined by the quantity $\frac{\omega_0\, v_\mathrm{p}}{c}$.

The term "normal distribution" is familiar from statistics, where it describes the distribution of many random variables. The reason it appears here is that the z-components of molecular velocities in a thermal gas (v_z) are themselves normally distributed, due to the random nature of molecular collisions and energy exchange.

Since there's a linear mapping between v_z and the frequency shift ($\omega - \omega_0$), this Gaussian distribution in velocity space directly translates into a Gaussian distribution in frequency space.

This Gaussian line shape is the hallmark of Doppler broadening in thermal ensembles.

Page 25:

Here we have a visual representation: **Gaussian Line Shape from Doppler Broadening.** This graph beautifully connects the velocity distribution to the resulting spectral line shape.

Let's examine the graph:

* The vertical axis is labeled "Relative Population / Intensity," which is normalized to a peak value of 1.0 at the center of the line.

* There are two horizontal axes.

* The bottom horizontal axis is labeled "v_s" (which is our v_z, the velocity component along the line of sight). It's marked with points $-2\,v_\mathrm{p}$, $-v_\mathrm{p}$, 0, v_p, $2\,v_\mathrm{p}$, where v_p is the most probable speed component $\left(\sqrt{\frac{2\,kT}{m}}\right)$. This axis represents the Maxwell-Boltzmann distribution of velocities.

* The top horizontal axis represents the angular frequency, ω. It's marked with points $\omega_0 - 2\Delta\omega$, $\omega_0 - \Delta\omega$, ω_0, $\omega_0 + \Delta\omega$, $\omega_0 + 2\Delta\omega$. This axis represents the resulting spectral line.

* The blue curve is the Gaussian profile. It shows that the peak intensity occurs at $\omega = \omega_0$, which corresponds to $v_\mathrm{z} = 0$ (molecules with no velocity component along the line of sight).

* The crucial link is stated: "**Linking** v_s and ω via: $v_\mathrm{s} = c\,\frac{\omega-\omega_0}{\omega_0}$". This is the linear transformation we've been using.

* An important annotation is "**(**$\Delta\omega = \frac{\omega_0\,v_\mathrm{p}}{c}$)". This $\Delta\omega$ is not the FWHM yet; it's a characteristic frequency scale, representing the Doppler shift produced by a molecule moving with speed v_p along the line of sight. The argument of the exponential in our Gaussian intensity profile was $\left(\frac{\omega-\omega_0}{\frac{\omega_0\,v_\mathrm{p}}{c}}\right)^2$, which can be written as $\left(\frac{\omega-\omega_0}{\Delta\omega_\mathrm{char}}\right)^2$ if we define $\Delta\omega_\mathrm{char} = \frac{\omega_0\,v_\mathrm{p}}{c}$. So, $\Delta\omega$ on this graph's top axis is this characteristic $\Delta\omega_\mathrm{char}$.

* Another annotation gives an "**Illustrative ratio:** $\frac{v_\mathrm{p}}{c} = 0.2$". This is a very large ratio, chosen for illustration to make the shifts clearly visible. In reality,

as we've discussed, $\frac{v_\mathrm{p}}{c}$ is typically much smaller, like 10^{-6}. If $\frac{v_\mathrm{p}}{c}$ were that small, the $\Delta\omega$ shifts would be tiny compared to ω_0, and the line would look extremely narrow on an absolute frequency scale, but it would still be Gaussian when zoomed in.

This graph nicely summarizes how the Gaussian distribution of v_z (bottom axis) maps directly, point by point, to a Gaussian intensity profile $I(\omega)$ (top axis) due to the linear Doppler shift.

Page 26:

Now that we have the Gaussian line shape, we need to quantify its width. This slide is about **Extracting the Doppler Width**.

* First bullet: "Define Doppler FWHM $\delta\omega_\mathrm{D}$ (delta omega sub D) as frequency interval where intensity drops to $\frac{1}{2}$ of peak." This is the standard definition of Full Width at Half Maximum (FWHM). We need to find the two frequencies, ω_upper and ω_lower, where $I(\omega) = \frac{I_0}{2}$, and then $\delta\omega_\mathrm{D} = \omega_\mathrm{upper} - \omega_\mathrm{lower}$. Due to the symmetry of the Gaussian, if ω_0 is the center, then $\omega_\mathrm{upper} = \omega_0 + \Delta\omega_\mathrm{HWHM}$ and $\omega_\mathrm{lower} = \omega_0 - \Delta\omega_\mathrm{HWHM}$, where $\Delta\omega_\mathrm{HWHM}$ is the Half Width at Half Maximum. So, $\delta\omega_\mathrm{D} = 2\Delta\omega_\mathrm{HWHM}$.

* Second bullet: "Solve:" We set the intensity $I(\omega)$ from our Gaussian profile equal to $\frac{I_0}{2}$:

$$I_0 \exp\left[-\left(\frac{c(\omega - \omega_0)}{\omega_0 v_\mathrm{p}}\right)^2\right] = \frac{I_0}{2}$$

Dividing by I_0, we get:

$$\exp\left[-\left(\frac{c(\omega - \omega_0)}{\omega_0 v_\mathrm{p}}\right)^2\right] = \frac{1}{2}$$

Let $\Delta\omega = |\omega - \omega_0|$ be the displacement from the line center where the intensity is half. So, $\Delta\omega$ is the HWHM. The equation becomes:

$$\exp\left[-\left(\frac{c\Delta\omega}{\omega_0 v_\mathrm{p}}\right)^2\right] = \frac{1}{2}$$

This is the equation presented on the slide.

* Third bullet: "Rearranging yields:" To solve for $\Delta\omega$, we take the natural logarithm of both sides:

$$-\left(\frac{c\Delta\omega}{\omega_0 v_\mathrm{p}}\right)^2 = \ln\left(\frac{1}{2}\right) = -\ln(2)$$

So,

$$\left(\frac{c\Delta\omega}{\omega_0 v_\mathrm{p}}\right)^2 = \ln(2)$$

Taking the square root of both sides:

$$\frac{c\Delta\omega}{\omega_0 v_\mathrm{p}} = \sqrt{\ln(2)}$$

Now, solving for $\Delta\omega$ (which is our $\Delta\omega_\mathrm{HWHM}$):

$$\Delta\omega = \frac{\omega_0 v_\mathrm{p}}{c}\sqrt{\ln(2)}$$

The Full Width at Half Maximum, $\delta\omega_\mathrm{D}$, is twice this value:

$$\delta\omega_\mathrm{D} = 2\Delta\omega = 2\left(\frac{\omega_0 v_\mathrm{p}}{c}\right)\sqrt{\ln(2)}$$

Or, as written on the slide:

$$\delta\omega_\mathrm{D} = 2\sqrt{\ln(2)}\,\frac{\omega_0 v_\mathrm{p}}{c}$$

This is the expression for the Doppler FWHM in terms of ω_0, v_p, c, and the constant factor $2\sqrt{\ln(2)}$. The term $\sqrt{\ln(2)}$ is approximately 0.8325, so $2\sqrt{\ln(2)}$ is approximately 1.665.

Page 27

We can make the expression for the Doppler width, $\delta\omega_\text{D}$, more explicit by substituting the definition of v_p.

* The first bullet reminds us to "**Substitute** $v_\text{p} = \sqrt{\frac{2\,kT}{m}}$":

Our formula for Doppler FWHM is $\delta\omega_\text{D} = 2\sqrt{\ln(2)} \cdot \frac{\omega_0 v_\text{p}}{c}$.

Substituting $v_\text{p} = \sqrt{\frac{2\,kT}{m}}$ into this, we get:

$\delta\omega_\text{D} = 2\sqrt{\ln(2)} \cdot \frac{\omega_0}{c} \cdot \sqrt{\frac{2\,kT}{m}}$.

We can combine the terms under the square root:

$$2\sqrt{\ln(2)} \cdot \sqrt{\frac{2\,kT}{m}} = \sqrt{4\ln(2) \cdot \frac{2\,kT}{m}} = \sqrt{\frac{8\,kT\ln(2)}{m}}$$

So, the expression for the Doppler width becomes:

$$\delta\omega_\text{D} = \frac{\omega_0}{c}\sqrt{\frac{8\,kT\ln(2)}{m}}$$

This is a very important and widely used formula. It clearly shows how the Doppler FWHM depends on:

* ω_0: the resonant frequency of the transition (linearly proportional). Higher frequency transitions have larger Doppler widths. * c: the speed of light (inversely proportional). * T: the absolute temperature (proportional to $\sqrt{T}$).

Higher temperatures mean wider Doppler widths. * m: the mass of the molecule (inversely proportional to $\sqrt{m}$). Lighter molecules have wider Doppler widths. * k: Boltzmann's constant. * $\ln(2)$: the natural logarithm of 2.

This formula is the cornerstone for calculating and understanding Doppler broadening in most spectroscopic applications involving gases.

Page 28:

This slide summarizes the **Mass & Temperature Dependence** of the Doppler width, $\delta\omega_{\mathrm{D}}$, based on the formula we just derived:

$$\delta\omega_{\mathrm{D}} = \frac{\omega_0}{c}\sqrt{\frac{8\,kT\ln(2)}{m}}$$

* First bullet: "**Linear in resonance frequency** ω_0. Higher-energy transitions broaden more." Since $E = \hbar\omega_0$, a higher energy transition means a larger ω_0. The formula shows $\delta\omega_{\mathrm{D}}$ is directly proportional to ω_0. So, for example, a UV transition will have a much larger Doppler width in frequency units than an infrared transition for the same species at the same temperature. This is because the fractional shift $\Delta\omega/\omega_0 = \frac{v_z}{c}$ is roughly the same, so if ω_0 is larger, $\Delta\omega$ will also be proportionally larger.

* Second bullet: "**Scales as** $\sqrt{T}$ (square root of T). Heating a gas increases Doppler width." The formula contains $\sqrt{T}$. This makes intuitive sense: higher temperature means the molecules have more kinetic energy, so their average speeds (and the width of their velocity distribution, v_{p}) are greater. A wider velocity distribution directly translates to a wider distribution of Doppler shifts, and thus a larger Doppler width.

* Third bullet: "**Inversely** $\propto \sqrt{m}$ (inversely proportional to square root of m). Light atoms (H, He) show largest widths." The formula contains $\frac{1}{\sqrt{m}}$. This also makes sense: at a given temperature, lighter particles move faster on

average than heavier particles (since kinetic energy $\frac{1}{2}mv^2$ is related to T). Faster speeds mean larger Doppler shifts. Therefore, for a given transition frequency and temperature, hydrogen (H) or helium (He) will exhibit significantly larger Doppler widths compared to, say, a heavy molecule like SF_6 (sulfur hexafluoride).

* Fourth bullet: "**Expressed with molar quantities for convenience:**" Often, it's more convenient to work with molar mass M (in kg/mol) rather than the mass of a single molecule m (in kg), and the ideal gas constant R instead of Boltzmann's constant k. We know that

$$R = N_{\mathrm{A}}k$$

(where N_{A} is Avogadro's number) and

$$M = N_{\mathrm{A}}m.$$

So,

$$\frac{k}{m} = \frac{R/N_{\mathrm{A}}}{M/N_{\mathrm{A}}} = \frac{R}{M}.$$

Substituting $\frac{k}{m} = \frac{R}{M}$ into our Doppler width formula:

$$\delta\omega_{\mathrm{D}} = \frac{\omega_0}{c}\sqrt{\frac{8\,RT\ln(2)}{M}}$$

The slide presents this slightly rearranged as:

$$\delta\omega_{\mathrm{D}} = \frac{2\omega_0}{c}\sqrt{\frac{2\,RT\ln(2)}{M}}$$

Let's check if these are equivalent:

$$\frac{2\omega_0}{c}\sqrt{\frac{2\,RT\ln(2)}{M}} = \frac{\omega_0}{c}\sqrt{\frac{4\times 2\,RT\ln(2)}{M}} = \frac{\omega_0}{c}\sqrt{\frac{8\,RT\ln(2)}{M}}.$$

Yes, they are identical. This form using molar mass M (in kg/mol) and the gas constant R is often very practical for calculations.

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Continuing with practical forms of the Doppler width formula:

- First bullet: $R = 8.314\,462\,618\,\mathrm{J\,mol^{-1}\,K^{-1}}$ (Joules per mole per Kelvin) – gas constant. This is the standard value of the molar gas constant.

- Second bullet: M – molar mass (kg mol^{-1} (kilograms per mole)). It's very important to be consistent with units. If R is in SI units (J $\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$), and T is in Kelvin, then M *must* be in kilograms per mole for the formula

$$\delta\omega_{\mathrm{D}} = \frac{\omega_0}{c}\sqrt{\frac{8\,RT\ln(2)}{M}}$$

to yield $\delta\omega_{\mathrm{D}}$ in radians per second (if ω_0 is in rad/s and c in m/s). Often, molar masses are tabulated in grams per mole (g/mol). If you use M in g/mol, you must include a conversion factor of 1000 (since 1 kg/mol = 1000 g/mol).

- Third bullet: **Numeric form (convert to frequency** ν (nu)): Spectroscopists often work with linear frequency ν (in Hertz, Hz) rather than angular frequency ω (in rad/s), where

$$\omega = 2\pi\nu.$$

So,

$$\delta\nu_{\mathrm{D}} = \frac{\delta\omega_{\mathrm{D}}}{2\pi}.$$

Substituting $\delta\omega_{\mathrm{D}}$:

$$\delta\nu_{\mathrm{D}} = \left(\frac{\omega_0}{2\pi c}\sqrt{\frac{8\,RT\ln(2)}{M}}\right) = \frac{\nu_0}{c}\sqrt{\frac{8\,RT\ln(2)}{M}}.$$

The slide provides a convenient numeric formula:

$$\delta\nu_\text{D} = 7.16 \times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}} \quad \text{[Hz]}.$$

Let's analyze this. This formula implies that the constant 7.16×10^{-7} must incorporate $\frac{1}{c}\sqrt{8\,R\ln(2)}$ and potentially a unit conversion factor if M is not in kg/mol.

Let's calculate

$$\frac{1}{c}\sqrt{8\,R\ln(2)}:$$

$c \approx 2.99792458 \times 10^8$ m/s $R \approx 8.31446$ J mol^{-1} K^{-1} $\ln(2) \approx 0.693147$ So,

$$\frac{1}{c}\sqrt{8\,R\ln(2)} = \frac{1}{2.99792458 \times 10^8} \times \sqrt{8 \times 8.31446 \times 0.693147}$$

$$= \frac{1}{2.99792458 \times 10^8} \times \sqrt{46.097}$$

$$= \frac{1}{2.99792458 \times 10^8} \times 6.7895$$

$$\approx 2.2647 \times 10^{-8} \quad \text{(with } M \text{ in kg/mol)}.$$

The constant in the slide is 7.16×10^{-7}. Let's see the ratio:

$$\frac{7.16 \times 10^{-7}}{2.2647 \times 10^{-8}} \approx 31.61.$$

This value, 31.61, is very close to $\sqrt{1000}$ (which is ≈ 31.62). This means that the numeric formula

$$\delta\nu_\text{D} = 7.16 \times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}}$$

assumes that the molar mass M is given in **grams per mole (g/mol)**, not kg/mol. If M is in g/mol, then

$$M_{\text{kg}} = \frac{M_{\text{g/mol}}}{1000}.$$

So,

$$\sqrt{\frac{1}{M_{\text{kg}}}} = \sqrt{\frac{1000}{M_{\text{g/mol}}}} = \sqrt{1000}\sqrt{\frac{1}{M_{\text{g/mol}}}}.$$

Thus, the numeric constant

$$7.16 \times 10^{-7} = \frac{1}{c}\sqrt{8\,R\ln(2) \times 1000}$$

if M is in g/mol in the $\sqrt{\frac{T}{M}}$ term. Or, more simply,

$$7.16 \times 10^{-7} = \left(\frac{1}{c}\sqrt{8\,R\ln(2)}\right)\sqrt{1000}.$$

$(2.2647 \times 10^{-8}) \times \sqrt{1000} \approx (2.2647 \times 10^{-8}) \times 31.62277 \approx 7.158 \times 10^{-7}$. This matches!

Crucial clarification for students: When using the numeric formula

$$\delta\nu_{\text{D}} = 7.16 \times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}} \quad [\text{Hz}],$$

ν_0 must be in Hz, T in Kelvin, and M must be the molar mass in grams per mole (g/mol). This is a common convention for such practical formulas but always double-check the units assumed for M.

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Let's apply this with a **Worked Example 1 – Lyman-α (Vacuum-UV)**. The Lyman-alpha transition in atomic hydrogen is a fundamental spectral line.

* **Transition:** $1s \rightarrow 2p$ in atomic H. This is the lowest energy transition in the Lyman series of hydrogen, from the $n = 1$ ground state to the $n = 2$ excited state.

* $\lambda = 121.6\,\text{nm} \Rightarrow \nu_0 = 2.47 \times 10^{15}\,\text{s}^{-1}$ (or Hz). The wavelength λ (lambda) of Lyman-alpha is approximately $121.6\,\text{nm}$. This is in the vacuum ultraviolet (VUV) region of the spectrum because air absorbs strongly at these wavelengths. The corresponding rest frequency ν_0 (nu naught) is $\frac{c}{\lambda}$.

$$\nu_0 = \frac{2.99792458 \times 10^8\,\text{m/s}}{121.6 \times 10^{-9}\,\text{m}} \approx 2.4654 \times 10^{15}\,\text{Hz}.$$

The slide uses $\nu_0 = 2.47 \times 10^{15}\,\text{s}^{-1}$, which is a good rounded value.

* **Parameters:** $T = 1000\,\text{K}$, $M = 1\,\text{g/mol}$. We consider atomic hydrogen (H, not H_2) at a temperature of $1000\,\text{K}$. This is a high temperature, typical of some plasmas or astrophysical environments. The molar mass M for atomic hydrogen is approximately $1\,\text{g/mol}$. (More precisely, about $1.008\,\text{g/mol}$.)

* **Compute:** We use the numeric formula from the previous page:

$$\delta\nu_\text{D} = 7.16 \times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}} \quad [\text{Hz}],$$

remembering M is in g/mol.

$$\delta\nu_\text{D} = (7.16 \times 10^{-7}) \cdot (2.47 \times 10^{15}\,\text{Hz}) \cdot \sqrt{\frac{1000\,\text{K}}{1\,\text{g/mol}}}$$

$$\delta\nu_\text{D} = (7.16 \times 10^{-7}) \cdot (2.47 \times 10^{15}) \cdot \sqrt{1000}$$

Since $\sqrt{1000} \approx 31.62277$,

$$\delta\nu_\text{D} \approx (7.16 \times 10^{-7}) \cdot (2.47 \times 10^{15}) \cdot 31.62277$$

$$\delta\nu_{\text{D}} \approx (1.76852 \times 10^{9}) \cdot 31.62277$$

$$\delta\nu_{\text{D}} \approx 5.590 \times 10^{10}\ \text{Hz}.$$

The slide gives the result as **5.6 × 10^{10} Hz**. This matches our calculation very well. So, the Doppler FWHM for Lyman-alpha at 1000 K is about 56 Gigahertz. This is a substantial broadening.

* **Convert to wavelength width:** We'll see this calculation on the next slide. Spectroscopists often want the width in wavelength units (e.g., nanometers or picometers) if they are using a grating spectrometer that disperses by wavelength.

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Continuing with the Lyman-alpha example, we now convert the Doppler width from frequency units ($\delta\nu_{\text{D}}$) to wavelength units ($\delta\lambda_{\text{D}}$).

The relationship between frequency ν and wavelength λ is $\nu = \frac{c}{\lambda}$.

To find the relationship between small changes $\delta\nu$ and $\delta\lambda$, we can differentiate:

$$|d\nu| = |-\frac{c}{\lambda^2}\,d\lambda| = \frac{c}{\lambda^2}|d\lambda|.$$

So, $\delta\nu = \frac{c}{\lambda^2}\delta\lambda$.

Rearranging for $\delta\lambda$, we get $\delta\lambda = \frac{\lambda^2}{c}\delta\nu$.

Or, more simply, for small widths, we can use the fractional relationship:

$$\frac{\delta\lambda}{\lambda_0} \approx \frac{\delta\nu}{\nu_0}.$$

So, $\delta\lambda_{\text{D}} \approx \lambda_0\left(\frac{\delta\nu_{\text{D}}}{\nu_0}\right)$.

Using the formula on the slide:

$$\delta\lambda_\text{D} = \frac{\lambda_0^2}{c}\,\delta\nu_\text{D}.$$

Given:

- $\lambda_0 = 121.6\,\text{nm} = 121.6 \times 10^{-9}\,\text{m}$ - $c \approx 2.99792458 \times 10^8\,\text{m/s}$ - $\delta\nu_\text{D} = 5.6 \times 10^{10}\,\text{Hz}$ (from the previous slide)

$$\delta\lambda_\text{D} = \left[\frac{(121.6 \times 10^{-9}\,\text{m})^2}{2.99792458 \times 10^8\,\text{m/s}}\right] \times (5.6 \times 10^{10}\,\text{s}^{-1})$$

$$\delta\lambda_\text{D} = \left[\frac{1.478656 \times 10^{-14}\,\text{m}^2}{2.99792458 \times 10^8\,\text{m/s}}\right] \times (5.6 \times 10^{10}\,\text{s}^{-1})$$

$$\delta\lambda_\text{D} = [4.93226 \times 10^{-23}\,\text{m} \cdot \text{s}] \times (5.6 \times 10^{10}\,\text{s}^{-1})$$

$$\delta\lambda_\text{D} \approx 2.762 \times 10^{-12}\,\text{m}.$$

Converting this to nanometers:

1 nm = 10^{-9} m, so 1 m = 10^9 nm.

$$\delta\lambda_\text{D} \approx 2.762 \times 10^{-12}\,\text{m} \times \left(\frac{10^9\,\text{nm}}{1\,\text{m}}\right) = 2.762 \times 10^{-3}\,\text{nm}.$$

The slide gives the result as $\delta\lambda_\text{D} = 2.8 \times 10^{-3}$ nm.

Our calculated value of 2.762×10^{-3} nm rounds nicely to 2.8×10^{-3} nm.

This is 0.0028 nanometers, or 2.8 picometers.

Even though $56\,\text{GHz}$ sounds like a large frequency width, the corresponding wavelength width for this VUV transition is quite small in absolute terms, but it can be very significant compared to other broadening mechanisms or the resolving power of instruments.

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Let's look at a **Worked Example 2 – Sodium D Line (Visible)**. The sodium D lines are very famous yellow lines in the visible spectrum.

* First bullet: "**Transition:** $3s \to 3p$ in Na." These are transitions from the $3s$ ground state configuration to the $3p$ excited state configuration in atomic sodium. There are actually two closely spaced lines (a doublet, D1 and D2) due to spin–orbit coupling, but for calculating Doppler width, we can use an average wavelength.

* Second bullet: "$\lambda = 589.1\,\text{nm}$, $\nu_0 = 5.10 \times 10^{14}\,\text{s}^{-1}$." The average wavelength is around $589.1\,\text{nm}$ (often quoted as $589.0\,\text{nm}$ for D2 and $589.6\,\text{nm}$ for D1; $589.3\,\text{nm}$ is a good average, the slide uses $589.1\,\text{nm}$). This is in the yellow part of the visible spectrum. The corresponding rest frequency $\nu_0 = \frac{c}{\lambda}$.

$$\nu_0 = \frac{2.99792458 \times 10^8\,\text{m/s}}{589.1 \times 10^{-9}\,\text{m}} \approx 5.0889 \times 10^{14}\,\text{Hz}$$

The slide uses $\nu_0 = 5.10 \times 10^{14}\,\text{s}^{-1}$, which is a good rounded value.

* Third bullet: "**Cell at** $T = 500\,\text{K}$. Molar mass $M = 23\,\text{g/mol}$." We consider sodium vapor in a cell at a temperature of $500\,\text{K}$ (which is 227 °C). This temperature is needed to get a reasonable vapor pressure of sodium. The molar mass M for sodium (Na) is approximately $23\,\text{g/mol}$ (more precisely, 22.99 g/mol).

* Fourth bullet: "**Calculation:**" We use the numeric formula

$$\delta\nu_\text{D} = 7.16 \times 10^{-7}\,\nu_0 \sqrt{\frac{T}{M}}\,\text{Hz}$$

with M in g/mol.

$$\delta\nu_\text{D} = (7.16 \times 10^{-7}) \times (5.10 \times 10^{14}\,\text{Hz}) \times \sqrt{\frac{500\,\text{K}}{23\,\text{g/mol}}}$$

$$\delta\nu_\text{D} = (7.16 \times 10^{-7}) \times (5.10 \times 10^{14}) \times \sqrt{21.73913}$$

Since $\sqrt{21.73913} \approx 4.66252$,

$$\delta\nu_{\text{D}} \approx (7.16 \times 10^{-7}) \times (5.10 \times 10^{14}) \times 4.66252$$

$$\delta\nu_{\text{D}} \approx (3.6516 \times 10^{8}) \times 4.66252$$

$$\delta\nu_{\text{D}} \approx 1.7025 \times 10^{9}\,\text{Hz}$$

The slide gives the result as $\delta\nu_{\text{D}} = 1.7 \times 10^{9}\,\text{Hz}$. This matches our calculation perfectly. So, the Doppler FWHM for the sodium D line at $500\,\text{K}$ is about 1.7 Gigahertz.

Now for the wavelength width, $\delta\lambda_{\text{D}}$. Using

$$\delta\lambda_{\text{D}} \approx \lambda_0 \left(\frac{\delta\nu_{\text{D}}}{\nu_0}\right):$$

$$\delta\lambda_{\text{D}} \approx (589.1 \times 10^{-9}\,\text{m}) \times \frac{1.7 \times 10^{9}\,\text{Hz}}{5.10 \times 10^{14}\,\text{Hz}}$$

$$\delta\lambda_{\text{D}} \approx (589.1 \times 10^{-9}\,\text{m}) \times (3.3333 \times 10^{-6})$$

$$\delta\lambda_{\text{D}} \approx 1.9636 \times 10^{-12}\,\text{m} = 1.9636 \times 10^{-3}\,\text{nm}$$

The slide directly states $\delta\lambda_{\text{D}} = 1.0 \times 10^{-3}\,\text{nm}$. There appears to be a discrepancy here. My calculation, consistent with the $\delta\nu_{\text{D}}$ and ν_0 values provided, gives approximately $1.96 \times 10^{-3}\,\text{nm}$. The slide's value of $1.0 \times 10^{-3}\,\text{nm}$ is about half of that. Let me re-check my calculation using

$$\delta\lambda_{\text{D}} = \frac{\lambda_0^2}{c}\delta\nu_{\text{D}}:$$

$$\delta\lambda_{\text{D}} = \frac{(589.1 \times 10^{-9}\,\text{m})^2}{2.9979 \times 10^{8}\,\text{m/s}} \times (1.7 \times 10^{9}\,\text{Hz})$$

$$\delta\lambda_{\text{D}} = \frac{3.4703881 \times 10^{-13}\,\text{m}^2}{2.9979 \times 10^{8}\,\text{m/s}} \times (1.7 \times 10^{9}\,\text{s}^{-1})$$

$$\delta\lambda_{\text{D}} = (1.157596 \times 10^{-21}\,\text{m} \cdot \text{s}) \times (1.7 \times 10^{9}\,\text{s}^{-1})$$

$$\delta\lambda_\mathrm{D} = 1.9679 \times 10^{-12}\,\mathrm{m} = 1.968 \times 10^{-3}\,\mathrm{nm}$$

My calculation is consistent. It's possible the slide's value for $\delta\lambda_\mathrm{D}$ for sodium is a typo or uses a different convention not stated (e.g., HWHM in wavelength, though that would be unusual in this context without specification). For consistency with the derived formulas, the value should be closer to 1.97×10^{-3} nm. In a lecture, I would point this out and proceed with the consistently calculated value, or note that the slide's value might stem from a specific rounding or approximation not detailed. We will use the value derived from the $\delta\nu_\mathrm{D}$: approximately 1.97×10^{-3} nm.

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Our final example: **Worked Example 3 – CO_2 Infrared Vibration.** This takes us to molecular spectroscopy in the infrared region.

* First bullet: "**Transition within rovibrational manifold of CO_2 .**" Carbon dioxide (C O two) is a linear molecule and has characteristic vibrational modes. When these vibrations are excited, there are also associated rotational transitions, leading to a "rovibrational" spectrum. We are considering one such transition.

* Second bullet: "$\lambda = 10\,\mu\mathrm{m} \Rightarrow \nu_0 = 3.0 \times 10^{13}\,\mathrm{s}^{-1}$." A wavelength of $10\,\mu\mathrm{m}$, or $10 \times 10^{-6}\,\mathrm{m}$, is firmly in the mid-infrared region. This is a typical wavelength for CO_2 vibrational transitions, often used in CO_2 lasers and atmospheric sensing. The corresponding rest frequency $\nu_0 = \frac{c}{\lambda}$.

$$\nu_0 = \frac{2.99792458 \times 10^8\,\mathrm{m/s}}{10 \times 10^{-6}\,\mathrm{m}} \approx 2.9979 \times 10^{13}\,\mathrm{Hz}.$$

The slide uses $\nu_0 = 3.0 \times 10^{13}\,\mathrm{s}^{-1}$, an excellent rounded value.

* Third bullet: "**Room temperature** $T = 300\,\mathrm{K}$; $M = 44\,\mathrm{g\,mol}^{-1}$." We consider CO_2 gas at room temperature, approximately $300\,\mathrm{K}$ (27 °C). The molar mass M for CO_2 is: Carbon (≈12 g/mol) + 2 × Oxygen (≈16 g/mol each) = 12 + 32 = 44 grams per mole.

* Fourth bullet: "**Evaluate width:**" Again, using $\delta\nu_\text{D} = 7.16 \times 10^{-7}\,\nu_0\sqrt{\frac{T}{M}}$ [Hz], with M in g/mol. $\delta\nu_\text{D} = (7.16 \times 10^{-7}) \times (3.0 \times 10^{13}\,\text{Hz}) \times \sqrt{\frac{300\,\text{K}}{44\,\text{g mol}^{-1}}}$ $\delta\nu_\text{D} = (7.16 \times 10^{-7}) \times (3.0 \times 10^{13}) \times \sqrt{6.81818}$

Since $\sqrt{6.81818} \approx 2.61116$, $\delta\nu_\text{D} \approx (7.16 \times 10^{-7}) \times (3.0 \times 10^{13}) \times 2.61116$ $\delta\nu_\text{D} \approx (2.148 \times 10^{7}) \times 2.61116$ $\delta\nu_\text{D} \approx 5.608 \times 10^{7}$ Hz.

The slide gives the result as $\delta\nu_\text{D} = 5.6 \times 10^{7}$ Hz. This is an excellent match. So, the Doppler FWHM for this CO_2 IR transition at 300 K is about 56 Megahertz (MHz).

Now for the wavelength width, $\delta\lambda_\text{D}$. Using $\delta\lambda_\text{D} \approx \lambda_0\left(\frac{\delta\nu_\text{D}}{\nu_0}\right)$: $\delta\lambda_\text{D} \approx \frac{(10\times10^{-6}\,\text{m})\times(5.6\times10^{7}\,\text{Hz})}{3.0\times10^{13}\,\text{Hz}}$ $\delta\lambda_\text{D} \approx (10 \times 10^{-6}\,\text{m}) \times (1.8666 \times 10^{-6})$ $\delta\lambda_\text{D} \approx 1.8666 \times 10^{-11}$ m.

Converting to nanometers (1 m = 10^{9} nm): $\delta\lambda_\text{D} \approx 1.8666 \times 10^{-11}\,\text{m} \times 10^{9}\,\frac{\text{nm}}{\text{m}} = 1.8666 \times 10^{-2}$ nm.

The slide gives $\delta\lambda_\text{D} = 1.9 \times 10^{-2}$ nm. This matches our calculation very well (0.019 nm vs 0.0187 nm). This is 0.019 nanometers, or 19 picometers.

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Following the CO_2 example, this slide points out a very important trend: "**Note dramatic decrease in** $\delta\nu_\text{D}$ (delta nu sub D) as wavelength increases and mass becomes larger."

Let's re-examine our formula for $\delta\nu_\text{D}$:

$$\delta\nu_\text{D} = \frac{\nu_0}{c}\sqrt{\frac{8RT\ln(2)}{M}}$$

which is also $(7.16 \times 10^{-7})\, \nu_0 \sqrt{\frac{T}{M}}$.

And since $\nu_0 = \frac{c}{\lambda_0}$, we can also write it as:

$$\delta\nu_{\mathrm{D}} = \frac{1}{\lambda_0}\sqrt{\frac{8RT\ln(2)}{M}} \text{ (some constants if not using SI for } M\text{)}$$

Or, more directly from the numeric form: $\delta\nu_{\mathrm{D}}$ is proportional to $\frac{\nu_0}{\sqrt{M}}$.

Let's compare the three examples:

1. **H Lyman-α:** * $\lambda_0 = 121.6\,\text{nm}$ (short, VUV) ⇒ ν_0 is very high ($2.47 \times 10^{15}\,\text{Hz}$) * $M = 1\,\text{g/mol}$ (very light) * $\delta\nu_{\mathrm{D}} = 5.6 \times 10^{10}\,\text{Hz} = 56\,\text{GHz}$. (Largest frequency width)

2. **Na D-line:** * $\lambda_0 = 589.1\,\text{nm}$ (medium, visible) ⇒ ν_0 is medium ($5.1 \times 10^{14}\,\text{Hz}$) * $M = 23\,\text{g/mol}$ (medium mass) * $\delta\nu_{\mathrm{D}} = 1.7 \times 10^{9}\,\text{Hz} = 1.7\,\text{GHz}$. (Intermediate frequency width)

3. **CO_2 IR vibration:** * $\lambda_0 = 10\,\mu\text{m} = 10{,}000\,\text{nm}$ (long, infrared) ⇒ ν_0 is relatively low ($3.0 \times 10^{13}\,\text{Hz}$) * $M = 44\,\text{g/mol}$ (heavier) * $\delta\nu_{\mathrm{D}} = 5.6 \times 10^{7}\,\text{Hz} = 56\,\text{MHz}$. (Smallest frequency width)

The trend is clear:

* As wavelength λ_0 increases, the rest frequency ν_0 decreases. Since $\delta\nu_{\mathrm{D}}$ is proportional to ν_0, the Doppler width in frequency units decreases.

* As mass M increases, $1/\sqrt{M}$ decreases. Since $\delta\nu_{\mathrm{D}}$ is proportional to $1/\sqrt{M}$ (or $\sqrt{\frac{1}{M}}$), the Doppler width in frequency units also decreases.

So, for long-wavelength transitions (e.g., microwave, far-IR) and/or heavy molecules, the Doppler broadening $\delta\nu_{\mathrm{D}}$ will be significantly smaller than for short-wavelength transitions (e.g., UV, X-ray) and/or light atoms/molecules, assuming the same temperature. This is a key consideration when designing high-resolution spectroscopy experiments or interpreting astronomical data. For instance, to resolve fine features in heavy molecules in the microwave, Doppler broadening might be small enough not to obscure them, whereas for light molecules in the UV, it can be a dominant effect.

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Now let's make a **Gaussian vs. Lorentzian – Qualitative Contrast**. We've established that Doppler broadening leads to a Gaussian profile, while natural broadening (and also collisional broadening, which we'll discuss more later) leads to a Lorentzian profile. How do they differ qualitatively?

* First point: "**Gaussian (Doppler): rapid wing decay** $\propto \exp[-(\Delta\omega)^2]$ (proportional to exponential of minus delta omega squared)." The key term here is "rapid wing decay." The Gaussian function falls off extremely quickly as you move away from the line center (i.e., as the detuning $\Delta\omega = |\omega - \omega_0|$ increases). The presence of $(\Delta\omega)^2$ in the exponent of a negative exponential means that once $\Delta\omega$ exceeds the characteristic width, the function plummets towards zero very fast.

* Second point: "**Lorentzian (natural/collisional): slow wing decay** $\propto \frac{1}{(\Delta\omega)^2}$ (proportional to one over delta omega squared)." In contrast, the Lorentzian function has a "slow wing decay." It decreases as the inverse square of the detuning. While $\frac{1}{(\Delta\omega)^2}$ certainly goes to zero as $\Delta\omega \to \infty$, it does so much more slowly than the Gaussian's exponential decay. These are the "heavy tails" or "far wings" we mentioned earlier.

* Third point: This is a very practical and important consequence: "**Even when Doppler width overwhelms natural width near line center, far-wing measurements can reveal Lorentzian contribution.**" In many gas-phase experiments, the Doppler width (Gaussian) is significantly larger than the natural width (Lorentzian). This means that near the line center

(small $\Delta\omega$), the observed line shape will look predominantly Gaussian. The much narrower Lorentzian is essentially "hidden" or "smeared out" by the broader Gaussian. However, because the Gaussian wings fall off so rapidly, if you make very sensitive measurements far out in the wings of the spectral line (large $\Delta\omega$), you might reach a point where the Gaussian contribution has become negligible, but the more slowly decaying Lorentzian wings are still detectable. This allows experimentalists, in some cases, to "see" the underlying Lorentzian component by carefully analyzing the far wings of a line, even when the core of the line is Doppler-dominated. This can be crucial for determining natural lifetimes or collision rates.

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This slide provides a visual for the **Gaussian vs. Lorentzian – Qualitative Contrast**, reinforcing the points from the previous page.

We are looking at a graph comparing a Gaussian profile (labeled "Gaussian (Doppler)", typically shown in blue) and a Lorentzian profile (labeled "Lorentzian (Natural/Coll.)", typically shown in orange or red). Both are plotted as intensity versus frequency detuning ($\Delta\omega$), and both are normalized to have the same peak intensity (1.0) at $\Delta\omega = 0$. The FWHM (Full Width at Half Maximum) is also indicated, and in this illustrative plot, they appear to have roughly similar FWHMs to facilitate comparison of their shapes, especially in the wings.

Key observations from the graph:

- **Near the center (small $\Delta\omega$)**: Both profiles are peaked. The Gaussian might appear slightly more "pointed" or "sharper" at the very peak compared to the Lorentzian if they have the same FWHM, because the Lorentzian is flatter near its maximum.

- **In the wings (larger $\Delta\omega$)**: This is where the dramatic difference lies.
- The **Gaussian (blue) line** drops off very steeply. An arrow points to its wing, labeled "Rapid wing decay ∝ $\exp[-(\Delta\omega)^2]$". • The **Lorentzian**

(orange/red) line has much more extended wings. It falls off noticeably slower. An arrow points to its wing, labeled "Slow wing decay $\propto \frac{1}{(\Delta\omega)^2}$". You can clearly see that at, say, $\Delta\omega = 2$ or 3 times the FWHM, the Gaussian intensity is practically zero, while the Lorentzian still has a measurable intensity.

The text at the top reiterates the decay laws: Gaussian (Doppler): rapid wing decay $\propto \exp[-(\Delta\omega)^2]$. Lorentzian (natural/collisional): slow wing decay $\propto \frac{1}{(\Delta\omega)^2}$. And the crucial implication: "Even when Doppler width overwhelms natural width near line center, far-wing measurements can reveal Lorentzian contribution." This graph perfectly illustrates why: far enough out, the Gaussian vanishes, leaving only the Lorentzian if it's present.

This visual comparison is essential for developing an intuition about these fundamental line shapes.

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So far, we've treated Doppler broadening as if it produces a *pure* Gaussian line shape. However, this slide asks, and answers, **Why Pure Gaussian Is Not Exact**.

Real molecule with given v_z still possesses finite lifetime ⇒ intrinsic Lorentzian response around its Doppler-shifted center.

This is the crucial physical insight. Consider a single molecule, or more precisely, a group of molecules all having the *same* velocity component v_z along the line of sight. Due to their velocity v_z, their resonance frequency will be Doppler-shifted from ω_0 to some $\omega' = \omega_0\left(1 + \frac{v_z}{c}\right)$. However, these molecules *also* have a finite excited-state lifetime τ (and may also be undergoing collisions). This finite lifetime (or collisional interruption) means that even for this specific velocity group, their interaction with light is not infinitely sharp at ω'. Instead, this single velocity group will have its own intrinsic, homogeneous lineshape, which is a **Lorentzian** profile of width γ (gamma, related to $\frac{1}{\tau}$ and collision rates), centered at its Doppler-shifted frequency ω'. So, what we really have is not a collection of infinitely sharp lines at different Doppler-shifted frequencies, but a collection of *Lorentzian* lines, each centered at a different Doppler-shifted frequency ω' corresponding to a particular v_z.

Ensemble profile = convolution

To get the total observed line shape from the entire ensemble of molecules (with their Maxwell-Boltzmann distribution of velocities), we need to sum up all these individual Lorentzian profiles, each centered at its appropriate ω' and weighted by the probability of that ω' (or v_z) occurring. This mathematical operation of summing a shape function shifted by a distribution function is precisely a **convolution**. Specifically, the observed line shape is the convolution of: **Gaussian (motion)** ***Lorentzian (lifetime).*** *The Gaussian function here represents the distribution of the Doppler-shifted center frequencies* ω' (which is equivalent to the Maxwell-Boltzmann distribution of v_z values). The Lorentzian function represents the intrinsic homogeneous lineshape associated with each velocity group. The asterisk (\(\)) denotes the convolution operation.

Result called the Voigt profile.

This convolution of a Gaussian and a Lorentzian function is known as the **Voigt profile**. It is the most general lineshape for an optically thin, thermalized gas where both Doppler (inhomogeneous) and lifetime/collisional (homogeneous) broadening are present.

Need Voigt to analyse high-resolution spectra (stellar atmospheres, laser diagnostics, pressure broadening studies).

In many real-world applications where high precision is required, assuming a pure Gaussian (for Doppler) or a pure Lorentzian (if homogeneous broadening dominates) is insufficient. One must use the Voigt profile to accurately model the observed spectral lines. This is essential for:

Stellar atmospheres: Analyzing the light from stars to determine temperatures, pressures, and chemical compositions. The line shapes are classic Voigt profiles.

Laser diagnostics: For example, in combustion research, measuring species concentrations and temperatures in flames often involves fitting Voigt profiles to absorption or fluorescence spectra.

Pressure broadening studies: By fitting Voigt profiles, one can disentangle the Gaussian (temperature-dependent Doppler) width from the Lorentzian (pressure-dependent collisional) width, thereby studying collision dynamics.

So, while the Gaussian is an excellent first approximation for Doppler broadening, the Voigt profile is the more complete and accurate description when homogeneous broadening is also significant.

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Let's elaborate on the **Lorentzian Line Shape for a Single Velocity Class**, which is a key component of the Voigt profile.

First bullet: "Lifetime-limited response centred at $\omega' = \omega_0\left(1 + \frac{v_z}{c}\right)$:"

As we discussed, consider a sub-group of molecules all having the same velocity component v_z along the line of sight. Their natural resonance frequency ω_0 is Doppler-shifted to ω' (omega prime) in the lab frame, where $\omega' = \omega_0\left(1 + \frac{v_z}{c}\right)$. This ω' is the center of the spectral response for *this specific velocity group*.

The line shape function for this single velocity class, due to its finite lifetime (and any other homogeneous broadening like collisions), is a Lorentzian. The slide gives a normalized Lorentzian function $L(\omega - \omega')$ (capital L of omega minus omega prime) as:

$$L(\omega - \omega') = \frac{\gamma/2\pi}{(\omega - \omega')^2 + (\gamma/2)^2}$$

Let's break this down:

$L(\omega - \omega')$ is the line shape function, describing the response as a function of the lab frequency ω, centered at ω'.

γ (gamma) is the **total homogeneous damping constant**, which is the FWHM of this Lorentzian component. It includes contributions from natural broadening ($\gamma_{\text{natural}} = \frac{1}{\tau}$) and collisional broadening ($\gamma_{\text{collisional}}$, which is proportional to pressure). So, $\gamma = \gamma_{\text{natural}} + \gamma_{\text{collisional}}$.

The denominator $(\omega - \omega')^2 + (\gamma/2)^2$ is the standard Lorentzian form.

The numerator $(\gamma/2\pi)$ is a normalization factor. If you integrate $L(\omega - \omega')$ with respect to ω from $-\infty$ to $+\infty$, the result is 1. This means L is a probability density function in frequency space for that given ω'.

Second bullet clarifies γ: "γ – total homogeneous damping constant (includes natural + collisional)."

Third bullet: "**Area under** L equals 1; ensures energy conservation across broadened line."

So, for every v_z, there's a corresponding ω', and around that ω', there's a little Lorentzian packet of width γ. The Voigt profile sums these up.

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This slide, titled **"Lorentzian Line Shapes for Different Velocity Classes,"** provides a crucial visual for understanding how the Voigt profile is constructed.

The graph plots Line Shape $L(\omega - \omega')$ on the vertical axis against Frequency ω on the horizontal axis.

We see two distinct Lorentzian profiles:

- One, shown in **blue**, is peaked at a frequency ω'_1 (omega prime one). This Lorentzian corresponds to a group of molecules with a specific velocity component, say v_{z1}, which results in the Doppler-shifted center ω'_1. The label "$v_\mathrm{s} < 0$" (using v_s for v_z) suggests this might be for molecules moving away from the observer, leading to a red-shifted center $\omega'_1 < \omega_0$ if ω_0 is to the right.
- The other, shown in **red**, is peaked at a different frequency ω'_2 (omega prime two). This corresponds to another group of molecules with a different velocity component, say v_{z2}, resulting in a different Doppler-shifted center ω'_2. The label "$v_\mathrm{s} > 0$" suggests this might be for molecules moving towards the observer, leading to a blue-shifted center $\omega'_2 > \omega_0$ if ω_0 is to the left of ω'_2.

The key takeaway from this image is that the overall observed spectral line is formed by an infinite number of such Lorentzians, one for each possible value of v_z (and thus each ω'). Each of these Lorentzians has the *same intrinsic shape and width* γ, but their center frequencies ω' are distributed according to the Maxwell-Boltzmann distribution of velocities (which leads to a Gaussian distribution of ω' values).

The equation at the top right, $\omega' = \omega_0 \left(1 + \frac{v}{c}\right)$ (using v for v_z), reminds us how the center of each Lorentzian is determined.

The overall Voigt profile is the "envelope" or sum of all these infinitesimally weighted Lorentzians. If the Doppler effect is very strong (large spread in v_z), the centers ω' will be widely spread, and the sum will look Gaussian. If the Doppler effect is weak but the homogeneous width γ is large, the sum will look more Lorentzian. In between, you get the characteristic Voigt shape.

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Now we explicitly address **Building the Voigt Profile – Convolution Integral.**

- First bullet: "**Let** $G(\omega')$ = Gaussian distribution from Doppler." Here, $G(\omega')$ represents the probability density function for the *centers* of the Lorentzian profiles. Because $\omega' = \omega_0 \left(1 + \frac{v_\mathrm{z}}{c}\right)$ and v_z follows a Maxwell-Boltzmann (Gaussian) distribution, the distribution of these Doppler-shifted center frequencies ω' will also be Gaussian, centered at ω_0. Specifically,

$$G(\omega') = \frac{1}{\Delta\omega_{D,\mathrm{gauss}}\sqrt{\pi}} \exp\left[-\left(\frac{\omega' - \omega_0}{\Delta\omega_{D,\mathrm{gauss}}}\right)^2\right]$$

where $\Delta\omega_{D,\mathrm{gauss}}$ is related to our previously defined Doppler width parameters; for example, if $\Delta\omega_{D,\mathrm{gauss}} = \frac{\omega_0 v_\mathrm{p}}{c}$, then the prefactor is $\frac{c}{\omega_0 v_\mathrm{p}\sqrt{\pi}}$. This $G(\omega')$ tells us the relative number of molecular velocity classes whose resonant frequency is Doppler-shifted to ω'. This $G(\omega')$ needs to be normalized to integrate to 1 over all ω'.

- Second bullet: "**Observed intensity from all molecules:**" The total observed intensity $I(\omega)$ at a laboratory frequency ω is obtained by summing (integrating) the contributions from all possible Lorentzian packets. Each packet is centered at some ω', has a shape $L(\omega - \omega')$, and its contribution is weighted by $G(\omega')$, the probability of that ω' occurring. This is precisely the definition of a convolution integral:

$$I(\omega) = I_0 \int_{-\infty}^{+\infty} G\,(\omega')\, L(\omega - \omega')\, d\omega'$$

(Capital I of omega equals Capital I sub zero times the integral from minus infinity to plus infinity of Capital G of omega prime, times Capital L of omega minus omega prime, d omega prime). Here: • I_0 is a constant representing the total line strength or peak intensity. • ω' is the integration variable; it represents the center frequency of a Lorentzian component from a specific velocity class. We integrate over all possible center frequencies ω'. • $G(\omega')$ is the Gaussian distribution function of these center frequencies (due to the Doppler effect). • $L(\omega - \omega')$ is the normalized Lorentzian line shape function (due to homogeneous broadening like lifetime or collisions), centered at ω'. It describes how a specific velocity class (with center ω') contributes to the intensity at the observation frequency ω.

This convolution integral mathematically describes the Voigt profile. It combines the Gaussian broadening from the distribution of molecular velocities with the Lorentzian broadening intrinsic to each molecule.

- Third bullet: "**Insert explicit forms:**" The next step would be to plug in the actual mathematical expressions for $G(\omega')$ and $L(\omega - \omega')$ into this integral. This leads to a rather complex integral that, unfortunately, does not have a simple analytical solution in terms of elementary functions.

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This slide attempts to show the explicit form of the Voigt integral after inserting $G(\omega')$ and $L(\omega - \omega')$, but the OCR has unfortunately garbled the equation significantly. Let me reconstruct the conceptual form based on our definitions.

If we take: $G(\omega') = (A_\mathrm{G}) \cdot \exp\left[-\left(\frac{\omega' - \omega_0}{W_\mathrm{G}}\right)^2\right]$ (where A_G is a normalization constant and W_G is related to the Gaussian width, e.g., $W_\mathrm{G} = \frac{\omega_0 v_\mathrm{p}}{c}$) and $L(\omega - \omega') = \frac{A_\mathrm{L}}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2}$ (where $A_\mathrm{L} = \frac{\gamma}{2\pi}$ for normalization)

Then the Voigt profile integral $I(\omega)$ would be proportional to:

$$\int_{-\infty}^{+\infty} \exp\left[-\left(\frac{\omega' - \omega_0}{W_\mathrm{G}}\right)^2\right] \frac{1}{(\omega - \omega')^2 + \left(\frac{\gamma}{2}\right)^2} \, d\omega'$$

multiplied by various constants.

The specific prefactor shown in the OCR, $\mathcal{N} \frac{\gamma N_\mathrm{i} c}{2 v_\mathrm{p} \pi^{3/2} \omega_0^2}$, seems to be an attempt to gather all constants if one started from $n_\mathrm{i}(v_\mathrm{z})$ and did the full transformation and normalization. The key is the integral part, which is the convolution of the exponential of a quadratic (Gaussian) with the inverse of a quadratic (Lorentzian).

Due to the complexity of this integral, it's usually not evaluated analytically in closed form for general use. This leads to the next point:

* "**Numerical evaluation often uses Faddeeva function** $w(z)$."

The Voigt profile, or the convolution integral, can be expressed in terms of a special function known as the Faddeeva function, often denoted $w(z)$ or $W(z)$. The Faddeeva function is the complex-valued error function of a complex argument, scaled by an exponential factor. Specifically, $w(z) = \exp(-z^2)\,\mathrm{erfc}(-iz)$, where erfc is the complementary error function.

The Voigt profile $V(\omega; W_\text{G}, \gamma)$ is proportional to the real part of the Faddeeva function, $\Re[w(z)]$, where the complex argument z is a combination of the frequency detuning $(\omega - \omega_0)$, the Gaussian width parameter W_G, and the Lorentzian width γ. Specifically,

$$z = \frac{(\omega - \omega_0) + i(\gamma/2)}{W_\text{G}\sqrt{2}}$$

(if W_G is the standard deviation of the Gaussian in frequency)

Or, using parameters like the Doppler HWHM $\Delta\omega_{D,\text{HWHM}} = W_\text{G}\sqrt{\ln 2}$ and Lorentzian HWHM $\gamma/2$:

$$z = \frac{(\omega - \omega_0)}{\Delta\omega_{D,\text{HWHM}}}\sqrt{\ln 2} + i\frac{(\gamma/2)}{\Delta\omega_{D,\text{HWHM}}}\sqrt{\ln 2}$$

There are well-established algorithms and software libraries to compute the Faddeeva function accurately, which then allows for precise calculation and fitting of Voigt profiles in experimental data analysis.

So, while the integral looks daunting, computational tools based on functions like the Faddeeva function make working with Voigt profiles quite manageable in practice.

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Now let's discuss some **Practical Uses of the Voigt Profile.** Why is it so important to understand and be able to model this line shape?

- First bullet: "Separate temperature (Gaussian width) from pressure or lifetime effects (Lorentzian width)."

This is perhaps the most powerful application. The Voigt profile has two characteristic width parameters: one associated with the Gaussian component (let's call it $\Delta\omega_\text{G}$, the Doppler width) and one with the Lorentzian component ($\Delta\omega_\text{L} = \gamma$, the homogeneous width).

We know that $\Delta\omega_\text{G}$ depends on temperature (T) and molecular mass (m).

And $\Delta\omega_{\mathrm{L}}$ depends on natural lifetime (τ_{nat}) and collisional processes (which are often pressure-dependent).

By carefully fitting an observed spectral line to a Voigt profile, one can extract *both* $\Delta\omega_{\mathrm{G}}$ and $\Delta\omega_{\mathrm{L}}$. From $\Delta\omega_{\mathrm{G}}$, one can determine the temperature of the gas (if m is known). From $\Delta\omega_{\mathrm{L}}$, one can gain information about lifetimes or collision rates (and thus pressure if the collisional broadening coefficient is known). This ability to disentangle different physical contributions from a single line shape is incredibly valuable.

- Second bullet: "Essential in:"

The Voigt profile is indispensable in a variety of fields:

- Third bullet: "Stellar atmosphere diagnostics (extract T & p layers)."

When we observe the light from a star, the absorption lines in its spectrum (Fraunhofer lines, for example) are formed in the star's atmosphere. These lines are broadened by the thermal motion of atoms/ions (Doppler broadening, giving Gaussian component) and by collisions and natural lifetimes (giving Lorentzian component). By fitting Voigt profiles to these stellar lines, astronomers can deduce the temperature, pressure, and even elemental abundances at different layers of the star's atmosphere.

- Fourth bullet: "Gas lasers & combustion monitoring (in-situ T, species concentration)."

In engineering and research, for example, in characterizing gas lasers or studying combustion processes, laser absorption spectroscopy is a key diagnostic. The absorption lines of various species (e.g., fuel, oxidizer, combustion products like H_2O, CO_2) are Voigt profiles. Fitting these allows for non-intrusive (in-situ) measurement of local gas temperature (from the Gaussian width) and species concentration (from the integrated line area, once T and p are known to get line strength). This is crucial for understanding and optimizing combustion, or for characterizing laser gain media.

- Fifth bullet: "Calibration of high-precision frequency references."

For metrology and frequency standards, understanding the precise line shape of atomic or molecular transitions is critical. Even small asymmetries or deviations from simpler models can lead to errors in defining a frequency. Voigt profile analysis helps to accurately determine the line center and quantify various broadening contributions, leading to more robust and accurate frequency references.

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Continuing with the practical uses of the Voigt profile:

- The bullet point here states: "**Accurate line-shape modelling improves trace-gas detection limits and climate remote-sensing retrievals.**" This highlights two more important application areas.

- **Trace-gas detection:** When trying to detect very small amounts of a specific gas (e.g., pollutants in the atmosphere, impurities in a process gas), spectroscopists often look for its characteristic absorption lines. The ability to accurately model the shape of these lines (using Voigt profiles) allows for more sensitive detection. If you know the exact shape, you can use sophisticated fitting algorithms (like matched filtering) to pull a very weak signal out of noise, or to deconvolve it from overlapping lines of other species. If you use an incorrect line shape model, your estimate of the gas concentration could be significantly in error, or you might miss the gas entirely if its signal is weak.

- **Climate remote-sensing retrievals:** Satellites and ground-based instruments constantly monitor the Earth's atmosphere by looking at the absorption or emission of sunlight or infrared radiation by atmospheric gases like CO_2, methane, water vapor, ozone, etc. To retrieve accurate concentrations of these gases (which are crucial for climate models), scientists must very precisely model how these gases absorb and emit radiation at different altitudes (and thus different pressures and temperatures). This involves using extensive databases of spectroscopic parameters (like HITRAN) where line positions, strengths, and broadening coefficients (for Voigt profiles) are cataloged. An accurate Voigt line shape model is absolutely fundamental to these retrieval algorithms. Even small errors in the line shape can lead to significant biases in the retrieved atmospheric composition.

So, from fundamental physics to applied engineering and global monitoring, the Voigt profile plays a vital role.

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This slide, also titled "Slide 20: Practical Uses of the Voigt Profile," provides a beautiful graphical example: "**Stellar Fe I Line: Voigt Profile Fit and Component Analysis.**" This shows exactly what we've been discussing.

We are looking at a plot of "Normalized Flux" on the vertical axis versus "Wavelength Offset ($\Delta\lambda$)" on the horizontal axis. The flux is normalized so that the continuum (the light level away from the absorption line) is at 1.0. The wavelength offset is relative to the line center.

Let's look at the components:

* **Measured Data (Fe I line):** These are shown as grey circular markers. They represent the actual observed flux from a star at different wavelengths across an iron (Fe I means neutral iron) absorption line. You can clearly see an absorption dip.

* **Voigt Profile Fit:** This is shown as a blue dashed line. It's the result of fitting a Voigt profile model to the measured data points. Notice how well the Voigt fit (labeled "$\mathrm{FWHM_V} \approx 2.11$" in arbitrary wavelength units for this plot) goes through the data, capturing the overall shape of the absorption line.

* **Gaussian Comp. (Component):** This is shown as a green dotted line. This is the Gaussian part of the Voigt profile that was determined from the

fit. It's labeled "$\text{FWHM} = 1.50$, Temperature related". This width is primarily due to the Doppler broadening from the thermal motion of iron atoms in the star's atmosphere.

* **Lorentzian Comp. (Component):** This is shown as a red dash-dotted line. This is the Lorentzian part of the Voigt profile from the fit. It's labeled "$\text{FWHM} = 1.00$, Pressure related". This width is due to homogeneous broadening effects like collisions (pressure broadening) and the natural lifetime of the transition.

This plot is extremely instructive. It visually demonstrates how the observed stellar absorption line (the grey dots) is not purely Gaussian or purely Lorentzian, but a Voigt profile (blue line). And, critically, the fitting process allows us to *decompose* this Voigt profile into its underlying Gaussian (green) and Lorentzian (red) contributions.

From the widths of these components, astrophysicists can then infer the temperature and pressure conditions in the region of the star's atmosphere where this iron line is formed. This is a cornerstone of quantitative stellar spectroscopy.

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Now, let's summarize the **Key Takeaways** from our discussion on Doppler broadening.

* First bullet: "**Doppler broadening arises from Maxwellian velocity spread; yields Gaussian FWHM**"

This is the fundamental origin: atoms or molecules in a gas are moving with a distribution of velocities (Maxwell-Boltzmann). Each velocity component along the line of sight causes a Doppler shift in the resonant frequency. The ensemble of these shifted frequencies results in a broadened spectral line that has a Gaussian shape.

The Full Width at Half Maximum (FWHM) of this Gaussian profile, which we denoted $\delta\omega_{\mathrm{D}}$ (delta omega sub D), is given by the formula:

$$\delta\omega_{\mathrm{D}} = \frac{\omega_0}{c}\sqrt{\frac{8kT\ln 2}{m}}$$

(delta omega sub D equals omega naught over c, times the square root of 8 k T natural log of 2, all over m). This formula encapsulates the dependence on the rest frequency ω_0, temperature T, and molecular mass m. Remember k is Boltzmann's constant, and c is the speed of light.

* Second bullet: "**Width grows with** $\sqrt{T}$ (square root of T) and shrinks with $\sqrt{m}$ (square root of m)."

These are the key dependencies extracted directly from the formula: * Higher temperature (T) leads to faster average molecular speeds, a wider velocity distribution, and thus a proportionally larger Doppler width (scales as $\sqrt{T}$). * Heavier mass (m) leads to slower average molecular speeds at a given temperature, a narrower velocity distribution, and thus a proportionally smaller Doppler width (scales as $\frac{1}{\sqrt{m}}$ or inversely with $\sqrt{m}$). These dependencies are intuitive and crucial for predicting and interpreting Doppler widths in various systems.

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Continuing with our **Key Takeaways**:

* First bullet: "**Observed profile often a Voigt convolution of Gaussian (motion) and Lorentzian (homogeneous) components.**" While Doppler broadening itself gives a Gaussian profile, we must remember that other broadening mechanisms are usually present simultaneously. Homogeneous broadening mechanisms, such as natural lifetime broadening and collisional (pressure) broadening, lead to a Lorentzian profile. When both types of broadening are significant, the actual observed

spectral line shape is a **Voigt profile**. The Voigt profile is mathematically the convolution of the Gaussian profile (arising from the distribution of Doppler shifts due to molecular motion) and the Lorentzian profile (arising from homogeneous effects that are the same for all molecules, regardless of their velocity, but specific to their own Doppler-shifted frame).

* Second bullet: "**Accurate determination of physical conditions demands disentangling these mechanisms via line-shape analysis.**" This underscores the practical importance of understanding these line shapes. If we want to use spectroscopy to accurately measure physical parameters of a system – such as temperature, pressure, species concentrations, or even gas flow velocities (from bulk Doppler shifts) – we often need to perform a careful line-shape analysis. This involves fitting the observed spectral data to an appropriate model, typically a Voigt profile. By doing so, we can "disentangle" the contributions from different broadening mechanisms. For instance, we can separate the Gaussian width (which tells us about temperature) from the Lorentzian width (which can tell us about pressure or lifetimes). Without this detailed line-shape analysis, our interpretation of spectroscopic data could be flawed, leading to inaccurate conclusions about the physical conditions of the system under study.

This concludes our detailed look into Doppler broadening and its context within overall spectral line shapes. It's a fundamental concept with far-reaching implications in many areas of physics, chemistry, engineering, and astronomy. Thank you.